THE PHILIPPINE

# JOURNAL OF SCIENCE

ALVIN J. COX, M. A., PH. D.
GENERAL EDITOR

## SECTION A
## CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

EDITED WITH THE COÖPERATION OF
H. C. BRILL, PH. D.; J. R. WRIGHT, PH. D.; G. W. HEISE, M. S.
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## CONTENTS

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A. CHEMICAL AND GEOLOGICAL SCIENCES
AND THE INDUSTRIES

VOL. XII JANUARY, 1917 No. 1

## THE FERMENTATION OF PHILIPPINE CACAO [1]

By HARVEY C. BRILL

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila*)

In an article by me[2] the statement was made that "the necessity for fermenting or sweating cacao is now generally acknowledged." This assertion "challenges trouble," declares the editor of Tropical Life,[3] since "no two experts seem agreed on this matter." However, the consensus of opinion appears to be with the above statement.[4]

Booth and Knapp, of Messrs. Cadbury Bros. Ltd., state:

> In general, we believe that if the planter only allows ripe pods to be gathered, ferments for a reasonable period, cures with care, and keeps the beans dry they will have the right appearance, and that he will be producing the best that the types of trees on his plantation will produce. * * * We understand that *unfermented* cacao finds purchasers, but fermented cacao, always obtains the higher price; unfermented beans are more difficult to shell, and they produce an inferior cocoa. Partially fermented beans suffer from the same defects.

W. H. Johnson, F. L. S., director of agriculture, Southern Provinces, Nigeria, says:

> Fermentation is more generally practiced than hitherto, but the period of fermenting and curing is too restricted.

S. H. Davies, of Messrs. Rowntree & Co., while insisting that the fermentation is due to the action of wild yeasts in the beginning and that the later action is due to true yeasts, believes

[1] Received for publication November 17, 1916.

[2] The enzymes of cacao, *This Journal, Sec. A* (1915), **10**, 123.

[3] Smith, Harold Hamel, *Trop. Life* (1916), **12**, 5.

[4] Booth, H. P., and Knapp, A. W., *Proc. Third Internat. Cong. Trop. Agr.* (1914), 225 et seq.

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that fermentation alone brings out the best flavor. Bainbridge and Davies [5] have shown that this flavor is due to the presence of an essential oil, which they believe is formed during the process of fermentation.

The only discordant voice raised at this Congress was that of Professor Perrot, of the Ecole Supérieure de Pharmacie, Paris, who reported an experiment in which he submitted 200 kilograms of cacao, sterilized at the Ivory Coast, to one of the French chocolate concerns. When roasted, this cacao became fragrant and in no respect was inferior to the products obtained by fermentation in the same region. He states that the pulp was removed by means of potassium carbonate solution and that the color was a fine violet. These two properties, the tenacity of the pulp and the violet color of the ribs, are characteristic of the unfermented cacao and are reasons for fermenting, since both are undesirable.

Knapp,[6] in discussing the Perrot method, states that the beans had a compact, cheesy interior, that they dried more slowly than the fermented beans, and that the process would be more costly than the present methods and would require skilled labor. He concludes with a plea for the encouragement of the use of the best-known methods of fermenting by the planters. In his book on cacao, van Hall [7] says of fermentation:

> All based on the same principle and have the same effect. This effect is the development of an essential oil, which gives the cocoa its peculiar aroma; the conversion of part of the bitter-tasting compound, so as to lessen the bitter taste; and, finally, the liberation of the theobromine, the substance which gives cocoa its peculiar tonic and stimulating properties.

These prominent authorities agree, with the exception of Professor Perrot, that the fermentation of cacao produces an improved product even though the changes taking place are not completely understood. To obtain various data that might throw some light on this process, the experiments recorded in this paper were performed. However, before this phase of the work is taken up, several other points will be discussed.

Recently I have had an inquiry from the Hershey Chocolate Company in which a method for the improvement of the color in poorly fermented cacao was requested.

[5] Bainbridge, J. S., and Davies, S. H., *Journ. Chem. Soc. London* (1912), 101, 2209.

[6] Knapp, A. W., *Trop. Life* (1915), 9, 227.

[7] Van Hall, C. J. J., Cacao. Macmillan & Co., London (1914), 201.

In my article dealing with the enzymes of cacao the statement was made that no glucoside-splitting enzyme was found in the forastero cacao examined at that time. Since this article appeared, I have made an investigation of the enzymes of the criollo variety and found that an emulsinlike enzyme which splits amygdalin, setting free hydrocyanic acid, exists in the latter. This same enzyme occurs in the forastero type, though not in as great activity. The enzymes found in the criollo and in the forastero types are identical in character, but in general they exist in somewhat larger quantities or more active forms in the former than in the latter. None was found that was peculiar to either type, and for this reason the results of the investigation of the enzymes of criollo are not recorded. The main difference is one of intensity of activity. The list stands as summarized for the forastero type in the preceding paper with the addition of an emulsinlike enzyme that exists in the unfermented seeds in somewhat greater activity than in the fermented product. The corrected list for the fermenting bean is casease, protease, oxidase, raffinase, diastase, invertase, and emulsinlike enzymes.

The Philippine Bureau of Agriculture, through its inspectors, has made a census of the various districts of the Islands for the purpose of obtaining information regarding the quantity of cacao produced and the methods of handling it. In only a few provinces was there more than enough raised for local consumption, but in most of them the presence of trees was noted, thus demonstrating that cacao will grow in many places in the Philippines. No conscious effort is made to ferment the beans, and the methods of preparation are very crude. These methods consist in drying the beans, without preliminary treatment, in the sun from three to six days, rubbing between the hands with ashes or rice husks to remove the pulp previous to placing in the sun, or mixing with rice hulls and sand and treading with the feet and washing to remove the pulp and then drying in the sun. While the quantity grown at present is small, the fact that the regions in which cacao can be grown are widespread throughout the Archipelago is encouraging. The experience of other cacao-growing countries lends hope to the belief that the Philippine Islands may become important as a cacao-growing country. Tables showing the production in other countries, as recorded by van Hall,[8] follow:

[8] Ibid., 499.

TABLE I.—*Production of cacao by countries, in tons of 1,000 kilograms.*

| Country. | 1908 | 1909 | 1910 | 1911 | 1912 | Increase or decrease of 1912 production over 1908 production. | | Average yield for 5 years. | Increase or decrease of average over 1908. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *Tons.* | *P. cent.* | | *Tons.* | *P. cent.* |
| Gold Coast | 12,946 | 20,534 | 23,112 | 40,357 | 39,500 | 26,554 | 205.1 | 27,292 | 14,346 | 110.9 |
| Ecuador | 32,119 | 31,564 | 36,305 | 38,804 | 35,500 | 3,381 | 10.5 | 34,858 | 2,739 | 8.5 |
| San Thome | 28,728 | 30,261 | 36,665 | 35,000 | 35,500 | 6,772 | 23.5 | 33,231 | 4,503 | 15.7 |
| Brazil | 32,956 | 33,818 | 29,158 | 34,994 | 30,000 | −2,956 | −9.0 | 32,177 | −779 | −2.3 |
| Trinidad | 21,370 | 23,390 | 26,231 | 21,220 | 18,900 | −2,470 | −11.1 | 22,224 | 854 | 3.9 |
| San Domingo | 19,005 | 14,818 | 16,623 | 19,828 | 20,900 | 1,895 | 9.1 | 18,235 | −770 | −4.0 |
| Venezuela | 16,303 | 16,848 | 17,251 | 17,381 | 12,500 | −3,803 | −23.3 | 16,057 | −246 | −1.5 |
| Grenada | 5,159 | 5,441 | 5,846 | 5,948 | 5,500 | 341 | 6.6 | 5,579 | 420 | 8.1 |
| Lagos | 1,388 | 2,276 | 2,978 | 4,471 | 3,500 | 2,112 | 152.2 | 2,923 | 1,535 | 110.6 |
| German colonies | 2,738 | 3,823 | 4,073 | 4,404 | 5,400 | 2,662 | 97.2 | 4,165 | 1,427 | 52.1 |
| Ceylon | 2,836 | 3,570 | 4,069 | 3,064 | 3,500 | 664 | 23.4 | 3,408 | 572 | 20.2 |
| Fernando Po | 3,001 | 2,726 | 2,349 | 3,000 | 2,300 | −701 | −23.3 | 2,675 | 326 | 10.8 |
| Jamaica | 2,694 | 3,216 | 1,743 | 2,783 | 3,400 | 706 | 26.2 | 2,767 | 73 | 2.7 |
| Java | 2,378 | 2,460 | 2,579 | 2,460 | 2,000 | −378 | −15.5 | 2,375 | −3 | −0.1 |
| Surinam | 1,699 | 1,897 | 2,043 | 1,565 | 1,000 | −699 | −41.1 | 1,641 | −58 | −3.4 |
| Haiti | 2,709 | 2,122 | 1,851 | 1,485 | 2,000 | −709 | −26.2 | 2,033 | −676 | −24.9 |
| French colonies | 1,421 | 1,372 | 1,575 | 1,364 | 1,500 | 79 | 5.5 | 1,446 | 25 | 1.8 |
| Cuba | 827 | 1,940 | 1,412 | 1,251 | 2,000 | 1,173 | 141.8 | 1,485 | 658 | 79.6 |
| St. Lucia | 615 | 553 | 743 | 940 | 900 | 285 | 46.3 | 750 | 135 | 21.9 |
| Belgian Congo | 612 | 769 | 902 | 681 | 800 | 188 | 30.9 | 753 | 141 | 23.0 |
| Dominica | 488 | 985 | 573 | 576 | 600 | 112 | 23.0 | 644 | 156 | 32.0 |
| Columbia | 621 | 730 | 297 | 400 | 400 | −221 | −35.6 | 490 | −131 | −21.1 |
| Costa Rica | 340 | 235 | 184 | 343 | 400 | 60 | 17.6 | 300 | −40 | −11.8 |
| Other countries | 800 | 1,000 | 1,000 | 1,500 | 1,500 | 700 | 87.5 | 1,160 | 360 | 45.0 |
| Total | 193,753 | 206,337 | 219,562 | 243,819 | 230,000 | 35,747 | 17.9 | 218,868 | 25,567 | 11.6 |

For the purpose of comparison and information the consumption of various countries is added.

TABLE II.—*Consumption of cacao by countries, in tons of 1,000 kilograms.*

| Country. | 1908 | 1909 | 1910 | 1911 | 1912 |
|---|---|---|---|---|---|
| United States | 42,615 | 53,379 | 50,315 | 58,965 | 57,000 |
| Germany | 34,352 | 40,725 | 43,941 | 50,855 | 55,100 |
| France | 20,445 | 23,254 | 25,068 | 27,340 | 26,900 |
| England | 21,052 | 24,264 | 24,082 | 25,396 | 28,100 |
| Holland | 15,821 | 19,387 | 19,187 | 23,536 | 24,900 |
| Switzerland | 5,821 | 6,684 | 9,089 | 9,852 | 10,300 |
| Spain | 6,580 | 5,980 | 5,517 | 6,379 | 5,300 |
| Other countries | 18,455 | 21,165 | 23,967 | 27,665 | 32,400 |
| Total | 165,141 | 194,838 | 201,166 | 229,988 | 240,000 |

The total increase for 1912 in per cent consumption based on the 1908 consumption is 45.3, while the increase in production based on the 1908 yield is 17.9 per cent.

The average increase in per cent consumption for the five years 1908–1912 based on the 1908 consumption is 24.9, while the increase in production calculated in the same manner is 11.6 per cent.

Comparing this increase in consumption, which in each case is practically double the increase in production, with the increase in production, it is at once apparent that the production is lagging behind. In other words, the present cacao-growing countries must increase their production more rapidly than they have been doing and new fields must be developed, or the rate of increase in consumption will decline. This disparity in increase of production and consumption cannot continue without an effect on the selling price. A rise in the selling price will lessen the sales and encourage interest in the cultivation. Reasoning in this manner, the growing of cacao on a large scale would appear to be a profitable venture for the Philippine Islands to attempt.

Very few localities in the Philippine Islands at the present time produce enough cacao for local consumption. Pampanga and Iloilo Provinces are the most important exceptions. The former reports the presence of five thousand cacao trees in the vicinity of Mexico alone. The cacao raised in this region is of good quality and appearance and compares favorably with that grown elsewhere. Two varieties are grown, criollo and a very fair quality of forastero. In Table III are given some data regarding samples of these varieties examined by the Bureau of Science.

TABLE III.—*Average weight of fruits and seeds of Philippine cacao.*

| Type. | Number examined. | Weight of fruits. | | | Weight of seeds. | | | Weight of seeds ÷ weight of fruit. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Maximum. | Minimum. | Average. | Maximum. | Minimum. | Average. | Maximum. | Minimum. | Average. |
| | | *g.* | *g.* | *g.* | *g.* | *g.* | *g.* | *P. ct.* | *P. ct.* | *P. ct.* |
| Forastero | 60 | 481 | 136 | 281 | 116 | 48 | 69 | 38.1 | 14.4 | 24.6 |
| Criollo | 60 | 531 | 190 | 355 | 168 | 65 | 99 | 38.2 | 17.7 | 27.9 |

The average weight of the fruit and the percentage of the seeds in the criollo is considerably greater than for the forastero. This is accounted for by the fact that more careful selection has been made of this variety for planting. The forastero is much more common and less difficult to obtain. The planting of criollo should be encouraged.

The data in Table IV illustrate some fermentation experiments with these two varieties of cacao.

TABLE IV.—*Description of samples and methods of fermentation of cacao beans.*

| Sample. | Variety. | Duration of fermentation. | Wet beans. | After fermenting and drying. | After fermenting and drying, based on wet beans. | Loss due to fermenting and drying. | Loss due to fermenting alone. | After shelling. | Nibs,[a] based on wet cacao. | Nibs, based on dry fermented cacao. | Odor. | Color. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Days.* | *Grams.* | *Grams.* | *P. ct.* | *P. ct.* | *P. ct.* | *Grams.* | *P. ct.* | *P. ct.* | | |
| C-U | Criollo | none | 400 | 165 | 41.3 | 58.7 | None | 103 | 25.8 | 62.4 | Hardly developed at all | Fair. |
| C-2 | do | 2 | 400 | 151 | 37.8 | 62.2 | 3.5 | 115 | 28.8 | 76.6 | Better than C-U, but not very pronounced | Do. |
| C-4 | do | 4 | 400 | 131 | 32.8 | 67.2 | 8.5 | 99 | 24.8 | 75.6 | Better than C-2. Excellent | Good. Better than C-2. |
| C-5 | do | 5 | 400 | 137 | 34.3 | 65.7 | 8.0 | 106 | 26.5 | 77.4 | Better than C-4. Excellent | Good. Better than C-4. |
| C-6 | do | 6 | 400 | 131 | 32.8 | 67.2 | 8.5 | 103 | 25.8 | 78.6 | Not so good as C-5. Less pronounced | Do. |
| C-7 | do | 7 | 400 | 132 | 33.0 | 67.0 | 8.3 | 105 | 26.3 | 79.5 | About the same as C-6 | Do. |
| C-6-y a | do | 6 | 400 | 138 | 34.5 | 65.5 | 7.8 | 97 | 24.3 | 70.3 | Rather poor. Not exactly chocolatelike | Poor. |
| C-6-TD b | do | 6 | 400 | 138 | 34.5 | 65.5 | 7.8 | 85 | 21.3 | 61.6 | Slightly better than C-6-y. Not so good as C-7. | Do. |
| C-6-y-S c | do | 6 | 557 | 187 | 33.6 | 66.4 | 7.7 | 136 | 24.4 | 72.7 | Fair. Almost as good as C-7. Different in character. | Do. |
| C-6-TD-S d | do | 6 | 400 | 135 | 33.8 | 66.2 | 7.5 | 108 | 27.0 | 80.0 | Better than C-6. Not so good as C-7 | Do. |
| C-7-C e | do | 7 | 400 | 141 | 35.3 | 64.7 | 6.0 | 99 | 24.8 | 70.2 | Not so good as C-6 | Fair. |
| C-7-T f | do | 7 | 400 | 136 | 34.0 | 66.0 | 7.3 | 99 | 24.8 | 72.8 | Of pronounced chocolate character | Do. |
| C-7-A g | do | 7 | 280 | 104 | 37.1 | 62.9 | 4.2 | 75 | 26.5 | 72.1 | do | Do. |
| F-U | Forastero. | none | 400 | 195 | 48.8 | 51.2 | none | 139 | 34.8 | 71.3 | Chocolate odor only slightly developed | Poor. |
| F-2 | do | 2 | 400 | 193 | 48.3 | 51.7 | 0.5 | 158 | 39.5 | 81.9 | Slightly better than F-U | Fair. |
| F-4 | do | 4 | 400 | 187 | 46.8 | 53.2 | 2.0 | 162 | 40.5 | 86.6 | do | Do. |
| F-5 | do | 5 | 400 | 182 | 45.5 | 54.5 | 3.3 | 153 | 38.3 | 84.1 | More pronounced chocolate odor than F-U to F-4. | Good. |
| F-6 | do | 6 | 400 | 180 | 45.0 | 55.0 | 3.8 | 157 | 39.3 | 87.2 | More pronounced chocolate odor than F-U to F-4. Not so fine as C-4 and C-5. | Do. |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| F-7 | do | 7 | 400 | 180 | 45.0 | 55.0 | 3.8 | 151 | 37.8 | 83.3 | More pronounced chocolate odor than F-U to F-4. | Do. |
| F-6-y a | do | 6 | 355 | 171 | 48.2 | 51.8 | 0.6 | 136 | 38.3 | 80.0 | Similar to C-6-y | Poor. |
| F-6-TD b | do | 6 | 200 | 86 | 43.0 | 57.0 | 5.8 | 73 | 36.5 | 84.9 | Similar to F-6-y | Do. |
| F-7-C e | do | 7 | 400 | 186 | 46.5 | 53.5 | 2.3 | 157 | 39.3 | 84.4 | Fair. Not highly developed | Fair. |
| F-7-T f | do | 7 | 400 | 171 | 42.8 | 57.2 | 5.5 | 140 | 35.0 | 81.8 | Fair. Somewhat less developed than F-7-Tf | Do. |
| F-7-A g | do | 7 | 205 | 99 | 48.3 | 51.7 | 0.5 | 76 | 37.1 | 76.8 | Not so good as F-7-Tf | Do. |
| Average C-U to C-7. | Criollo | 4 | 400 | 141 | 35.3 | 64.7 | 4.8 | 105 | 26.3 | 75.0 | | |
| Average F-U to F-7. | Forastero | 4 | 400 | 186 | 46.6 | 53.4 | 2.2 | 153 | 38.3 | 82.4 | | |

[a] By nibs is meant the dry, shelled beans.

This cacao was fermented by placing the wet beans in beakers, at the top and bottom of which were layers of cotton to retain the juices given off when the beans underwent fermentation and to prevent the too rapid escape of the moisture from the beaker. Twice daily the beans were removed from the beakers and carefully stirred in order that they might ferment uniformly and that they might come in contact with the air. They were kept in an incubator at a temperature of 37.5° C. This was necessary, since the small bulk of seeds allowed the heat from the fermentation to escape so rapidly that, if left in the open air, the fermentation would have been very incomplete. Under these conditions the highest temperature reached by any of the samples was 45° C. The criollo fermented much more rapidly than the forastero. Active fermentation was practically complete at the end of four days, and a considerably finer product resulted, judging by the odor, color, and other organoleptic properties. More difficulty was experienced in fermenting forastero. The fermentation proceeded considerably more slowly, and the temperature did not rise high enough to kill the germ of the seeds in all cases; consequently there was a tendency to sprout. In larger masses of the beans the temperature would undoubtedly rise higher and the germ would be destroyed, but the above tendency illustrates the difference in the speed of fermentation of the two types under the conditions of the experiment.

(*a*) Samples *C–6–y* and *F–6–7* were sterilized by heating in hot water until the germ was killed and the activity of the enzymes destroyed. When the samples had become cool, yeast was added, and they were incubated.

(*b*) The treatment of samples *C–6–TD* and *F–6–TD* was identical in all respects with that of samples *C–6–y* and *F–6–7*, except that taka-diastase was added instead of yeast.

(*c*) Sample *C–6–y–S* had yeast added, but it was not sterilized.

(*d*) Sample *C–6–TD–S* had taka-diastase added, but it was not sterilized.

(*e*) Samples *C–7–C* and *F–7–C* had chloroform placed on the sterile cotton covering to prevent the introduction of yeast and of bacteria. From time to time additional amounts of chloroform were added to take the place of the volatilized portion.

(*f*) Samples *C–7–T* and *F–7–T* had toluene added instead of chloroform. The subsequent treatment was identical with that of samples *C–7–C* and *F–7–C*.

(*g*) Samples *C–7–A* and *F–7–A* had alcohol added instead of chloroform or toluene. The subsequent treatment was identical with that indicated in paragraphs "e" and "f."

Table V carries some further analytical data in regard to these samples of cacao. All these results are calculated on the basis of the water-free product in order that they may be directly comparable with each other and with the results listed in Table VI. All results were obtained from the shelled seeds.

TABLE V.—*Analytical data of Philippine cacao.*

[Numbers give percentages.]

| Sample No. | Fat. | Theobromine. | Albuminoids (N × 6.25). | Glucose. | Sucrose. | Starch. | Astringent matter. | Cellulose. | Extractive matter. | Ash. | Insoluble ash. | Alkalinity of ash from 1 gm. cacao in cc. N/10 acid. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C-U | 48.13 | 0.71 | 12.13 | 0.73 | 2.08 | 3.62 | 4.83 | 14.83 | 16.25 | 5.05 | 2.39 | 4.06 |
| C-2 | 52.27 | 1.27 | 12.81 | 0.63 | 0.85 | 5.14 | 4.31 | 14.13 | 12.88 | 5.57 | 2.16 | 3.39 |
| C-4 | 52.06 | 1.11 | 12.25 | 0.46 | 0.11 | 5.52 | 4.27 | 14.69 | 13.13 | 5.10 | 2.43 | 3.35 |
| C-5 | 51.00 | 0.90 | 12.06 | 0.45 | 0.00 | 5.41 | 4.04 | 15.71 | 11.88 | 4.63 | 2.30 | 3.26 |
| C-6 | 55.34 | 1.10 | 11.44 | 0.10 | 0.00 | 5.85 | 4.04 | 15.43 | 12.25 | 4.92 | 2.45 | 3.13 |
| C-7 | 53.13 | 0.84 | 12.19 | 0.36 | 0.00 | 5.91 | 3.65 | 15.36 | 11.25 | 4.70 | 1.80 | 2.72 |
| C-6-y | 56.69 | 0.84 | 11.38 | 0.27 | 0.00 | 4.58 | 2.88 | 11.12 | 11.08 | 2.95 | 1.63 | 2.77 |
| C-6-TD | 53.62 | 0.75 | 13.06 | 0.49 | 0.27 | 4.81 | 3.13 | 11.14 | 12.75 | 2.93 | 1.46 | 2.35 |
| C-6-y-S | 50.79 | 0.70 | 12.69 | 0.15 | 0.00 | 4.62 | 3.55 | 13.48 | 11.38 | 4.10 | 2.55 | 3.51 |
| C-6-TD-S | 50.11 | 0.80 | 13.43 | 0.15 | 0.45 | 4.26 | 4.11 | 17.91 | 12.83 | 4.60 | 2.60 | 3.30 |
| C-7-C | 50.08 | 1.06 | 12.94 | 0.39 | 0.56 | 3.96 | 2.96 | 14.26 | 11.58 | 5.12 | 2.12 | 2.70 |
| C-7-T | 46.12 | 1.10 | 13.19 | 0.77 | 0.22 | 5.17 | 3.27 | 14.86 | 13.50 | 5.22 | 2.58 | 2.52 |
| C-7-A | 45.64 | 1.20 | 12.75 | 0.92 | 0.10 | 5.36 | 3.59 | 14.63 | 13.88 | 4.90 | 2.32 | 3.82 |
| F-U | 43.67 | 0.70 | 12.88 | 0.91 | 1.71 | 2.33 | 6.20 | 14.78 | 17.13 | 4.93 | 2.42 | 4.17 |
| F-2 | 49.92 | 0.80 | 13.50 | 0.13 | 1.83 | 5.00 | 5.31 | 14.61 | 15.00 | 4.77 | 2.33 | 3.67 |
| F-4 | 49.93 | 1.05 | 13.00 | 0.02 | 1.38 | 5.18 | 4.83 | 13.94 | 15.00 | 4.98 | 2.42 | 3.74 |
| F-5 | 51.09 | 0.85 | 13.13 | 0.25 | 0.22 | 5.42 | 4.31 | 14.76 | 13.07 | 4.55 | 2.23 | 3.02 |
| F-6 | 52.21 | 0.88 | 13.91 | 0.21 | 0.45 | 5.49 | 4.20 | 14.21 | 14.13 | 4.68 | 2.20 | 2.82 |
| F-7 | 53.55 | 1.02 | 13.00 | 0.10 | 0.27 | 5.92 | 3.69 | 14.75 | 12.13 | 4.77 | 2.57 | 2.99 |
| F-6-y | 50.30 | 0.75 | 13.38 | 0.24 | 0.00 | 4.52 | 3.07 | 10.65 | 11.07 | 2.55 | 1.16 | 2.16 |
| F-6-TD | 55.99 | 1.00 | 13.88 | 0.05 | 0.40 | 5.07 | 3.35 | 10.71 | 8.85 | 3.25 | 1.38 | 2.03 |
| F-7-C | 46.29 | 1.08 | 13.50 | 0.33 | 0.64 | 4.15 | 5.09 | 14.39 | 14.85 | 5.27 | 2.12 | 2.51 |
| F-7-T | 48.36 | 0.80 | 13.75 | 0.44 | 0.30 | 4.18 | 3.55 | 14.88 | 12.03 | 5.00 | 2.24 | 2.91 |
| F-7-A | 41.67 | 0.85 | 13.69 | 0.87 | 0.61 | 4.56 | 3.55 | 14.44 | 12.50 | 4.98 | 2.22 | 2.78 |
| Average of C-U to C-7, inclusive | 51.99 | 0.97 | 12.15 | 0.46 | 0.51 | 5.24 | 4.19 | 14.69 | 12.96 | 4.99 | 2.22 | 3.32 |
| Average of F-U to F-7, inclusive | 50.06 | 0.88 | 13.24 | 0.27 | 0.98 | 4.89 | 4.76 | 14.51 | 14.41 | 4.78 | 2.36 | 3.40 |

[a] For general methods of analysis, see Parry, E. J., Foods and Drugs. Scott, Greenwood & Son, London (1911), 1, 20.

For purposes of comparison some figures taken from a paper by Ridenour [9] are entered in Table VI. I have recalculated these to the dry weight of the cacao in order that they may be directly comparable with the results of Table V.

[9] Ridenour, William E., *Am. Journ. Pharm.* (1895), 67, 207.

TABLE VI.—*Analytical data of cacao from various sources.*

[Numbers give percentages.]

| | Bahia. | Surinam. | Java. | Trinidad. | Ariba. | Curaçao. | Granada. | Tabasco. | Machalle. | Maracaybo. | Maximum. | Minimum. | Average. | Average for Philippine criollo. | Average for Philippine forastero. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fat | 44.77 | 43.44 | 47.64 | 46.61 | 46.00 | 39.42 | 46.57 | 51.75 | 49.75 | 44.77 | 51.75 | 39.42 | 46.07 | 51.99 | 50.06 |
| Theobromine | 1.14 | .98 | 1.22 | .90 | .91 | 1.20 | .79 | 1.17 | .81 | 1.09 | 1.22 | .79 | 1.02 | 0.97 | 0.88 |
| Albuminoids | 7.97 | 10.82 | 9.76 | 12.70 | 10.77 | 11.33 | 10.31 | 7.98 | 13.45 | 12.25 | 13.45 | 7.98 | 10.73 | 12.15 | 13.24 |
| Glucose | 1.13 | 1.33 | 1.30 | 1.47 | .44 | 2.94 | 1.91 | .95 | 1.70 | 1.15 | 2.94 | .44 | 1.45 | 0.46 | 0.27 |
| Sucrose | .54 | .37 | .54 | .34 | 6.76 | 1.67 | .58 | 2.76 | .49 | 1.44 | 6.76 | .34 | 1.45 | 0.51 | 0.98 |
| Starch | 8.01 | 3.81 | 5.45 | 5.32 | 1.67 | 4.08 | 6.61 | 3.57 | 1.43 | 1.79 | 8.01 | 1.43 | 4.17 | 5.24 | 4.89 |
| Lignin | 8.36 | 4.11 | 6.43 | 6.03 | 4.88 | 3.51 | 5.85 | 6.54 | 6.30 | 7.59 | 8.36 | 3.51 | 5.96 | | |
| Cellulose | 14.67 | 17.07 | 14.60 | 13.90 | 14.95 | 17.50 | 14.24 | 12.77 | 12.00 | 18.36 | 18.36 | 12.00 | 15.01 | 14.69 | 14.51 |
| Extractive | 9.56 | 14.21 | 9.39 | 8.88 | 9.56 | 13.61 | 10.29 | 9.51 | 9.56 | 7.20 | 14.21 | 7.20 | 10.18 | [a] 12.96 | 14.41 |
| Ash | 3.83 | 3.21 | 3.49 | 3.84 | 3.96 | 4.66 | 2.86 | 3.11 | 4.40 | 4.38 | 4.66 | 2.86 | 3.78 | 4.99 | 4.78 |

[a] Extractive matter direct.

In Table VI a comparison is made of the analytical data obtained for Philippine cacao and a number of foreign cacaos. This comparison places the former in a very favorable light in so far as such data are indicative of the quality of cacao.

An examination of the cacao butter was made to determine what changes, if any, took place in it with the variation in fermentation.

TABLE VII.—*Properties of cacao butter from Philippine cacao.*

| Sample No. | Saponification value. | Acid value cc. 0.1 *N* base per gm. oil. | Index of refraction. | Color. | Odor. |
|---|---|---|---|---|---|
| C-U | 191.5 | 0.10 | 1.4600 | Light yellow. Deeper than straw yellow. | Pronounced; somewhat harsh. |
| C-2 | 191.1 | 0.17 | 1.4599 | Somewhat deeper than C-U. | Similar to preceding. |
| C-4 | 193.8 | 0.27 | 1.4582 | Same as C-2 | Better than C-2. Faintly harsh. |
| C-5 | 194.3 | 0.23 | 1.4580 | do | Good; not so pronounced as C-4. |
| C-6 | 192.6 | 0.33 | 1.4579 | do | Pleasant; esterlike. |
| C-7 | 192.4 | 0.44 | 1.4579 | do | Do. |
| C-6-y | 193.9 | 0.13 | 1.4580 | do | Mild; not so characteristic as C-7. |
| C-6-TD | 194.8 | 0.15 | 1.4580 | do | Do. |
| C-6-y-S | 191.0 | 0.14 | 1.4580 | Slightly lighter than C-6-TD. | Do. |
| C-6-TD-S | 191.4 | 0.14 | 1.4580 | do | Do. |
| C-7-C | 192.2 | 0.15 | 1.4579 | Almost water white | Very mild; slightly sweet. |
| C-7-T | 193.6 | 0.21 | 1.4581 | do | Not so mild as C-7-C. |
| C-7-A | 191.7 | 0.18 | 1.4582 | Deeper yellow than C-7-C | Pleasant; chocolatelike. |
| F-U | 192.7 | 0.18 | 1.4585 | Same as C-U. Similar to C-2. | Pronounced; not so evident as C-U. |
| F-2 | 196.5 | 0.26 | 1.4590 | Somewhat deeper than F-U. | Similar to F-U. |
| F-4 | 198.5 | 0.53 | 1.4585 | do | Slightly better than F-2. |
| F-5 | 195.9 | 1.09 | 1.4582 | do | Good; better than preceding three. |
| F-6 | 196.6 | 1.27 | 1.4580 | Deeper yellow than F-5 | Esterlike; pleasant. |
| F-7 | 193.9 | 2.08 | 1.4581 | do | Do. |
| F-6-y | 192.4 | 0.17 | 1.4582 | Slightly lighter than F-7 | Faintly esterlike; less so than F-7. |
| F-6-TD | 193.7 | 0.25 | 1.4581 | Deeper yellow than F-6-y | Slightly harsher than F-6-y. |
| F-7-C | 193.6 | 0.22 | 1.4579 | Same as F-6-y | Not pronounced; pleasant. |
| F-7-T | 197.0 | 0.49 | 1.4581 | do | Very pleasant. |
| F-7-A | 191.6 | 0.18 | 1.4582 | do | Do. |
| Average for C-U to C-7, inclusive. | 192.6 | 0.26 | 1.4586 | | |
| Average for F-U to F-7, inclusive. | 195.7 | 0.90 | 1.4584 | | |

DISCUSSION

The loss in weight due to fermentation is given in Table IV. The criollo has the greater percentage of loss from fermentation. This is more apparent because the fermentation of the criollo was more nearly complete than the fermentation of the forastero. If perfect fermentation could be induced in the latter, the loss in it would undoubtedly approach that for criollo. However, a difference in the selling price of the fermented products would be made in favor of the criollo because of its superior quality, and this would still allow more profit to be made from the cultivation of the criollo than from that of the forastero. Then, too, the latter, because of its slowness in fermenting, is in greater danger of being spoiled by molding or by sprouting than is the former, and losses from this cause would be more apt to occur. On the other hand, the criollo samples examined had a larger average weight for the fruit, 531 grams, and a higher average yield of seeds, 27.9 per cent, than the forastero, which had an average weight of 481 grams and an average yield of 24.6 per cent of seeds. This would make the yields of dry, shelled seeds compare, criollo to forastero, as 1,089 to 1066; consequently, regardless of a difference in price in favor of criollo, the profit from its cultivation would be greater than from the cultivation of forastero, since the absolute yield of dry, shelled seeds, or nibs, is greater from the criollo than from the forastero.

The greater rapidity of the fermentation of the criollo is demonstrated by the loss in weight due to the fermentation. The maximum loss in weight has been reached at the end of the fourth day, while the forastero shows a maximum at the end of the sixth day. The intensity of the fermentation is likewise demonstrated by these same figures, for criollo shows a maximum of 8.5 per cent and forastero a maximum of 3.8 per cent. The changes effected by fermentation should be much less in the case of the latter, judged by the change in weight, and this is borne out by the less agreeable odor of the defatted [10] cacao and the cacao butter. The odor is most pleasant between the third and fourth days for the cacao butter and about the fourth day for the defatted cacao in the case of the criollo type, while the fifth and sixth days for the cacao butter and the

[10] By defatted cacao is here meant cacao from which all the fat has been etherized.

fifth and sixth days for the defatted cacao show the finest flavored product in the case of the forastero. But the product of this longer fermentation period for forastero does not equal that from criollo in quality.

The changes brought about by fermentation are hard to demonstrate by an analysis of the finished cacao. The changes are largely characterized by an improvement in its organoleptic properties. Bainbridge and Davies [11] believe that an essential oil is produced during fermentation. In their investigation on fermented arriba from Ecuador, they obtained 24 grams of an essential oil from 2,000 kilograms of cacao. Ordinary analytical chemical methods would not suffice for the detection of so minute quantities. The theobromine shows no regular variation. Sack [12] claims that one of the results of fermentation is the splitting of a glucoside with the formation of theobromine and cacao-red. The results obtained in this investigation do not corroborate his conclusions.

The glucose and sucrose content change with the degree of fermentation, the latter in several cases being zero, while the former first decreases and then shows a slight increase. This increase is due to the action of diastase on the starch. The sugar usually listed as glucose in the analysis of fermented cacao is doubtless largely maltose, the product of the action of diastase on starch. The percentage of starch does not undergo a decisive change. The apparently smaller amount in *C–U* and *F–U* is partly accounted for by the fact that these samples have not lost juices through fermentation. I believe a change has taken place in the character of the starch by the fermentation and that this makes itself apparent in the so-called break of fermented cacao.

A change in the percentage of astringent matter with length of fermentation is the most apparent change that can be demonstrated by analytical data. The amount decreases with the length of fermentation and accounts for part of the improvement in the flavor of the product. The superiority of the criollo over the forastero is apparent when a comparison is made of the quantities of astringent matters present in the two.

The difference in the cellulose content of the fermented and unfermented samples can be explained by the fact that the former has lost juices by fermentation while the latter still retains these. The same explanation holds for the difference in extractive matter. Van Hall [13] states that good cacao should

[11] Loc. cit. [12] *Bull Dept. Agr. Surinam,* 10. [13] Loc. cit.

show 12 per cent or more extractive matter. The Philippine product averages slightly more than this.

The free acidity of the cacao butter increases with the duration of the fermentation. Criollo is superior to forastero in this respect also. In spite of the greater intensity of the fermentation, it shows less free acidity than does forastero, the ratio being 0.26 cubic centimeter to 0.90 cubic centimeter 0.1 $N$ alkali, respectively. The slight change in the acidity of the cacao butter with the greater length of fermentation is confirmatory of the conclusion reached by me [14] that Philippine cacao does not contain a lipase.

For the purpose of making a further investigation of the fermentation processes, certain special samples were prepared. These are described on page 8. An extended discussion of these samples is hardly necessary, since in no case is the quality of the final product equal to that obtained by the use of the ordinary methods. Samples *C–6–y* and *F–6–y* had yeast added to them after they had first been sterilized to destroy the activity of the enzymes. In the sterilization of the seeds care was taken to prevent cooking and at the same time effectively to sterilize. The final product did not equal *C–6* or *F–6* in excellence of odor, color, or break. It would appear that yeasts alone do not produce the desired changes. Bainbridge and Davies [15] make the statement that wild yeasts from the pods and stems first act on the pulp and that in the latter stages of fermentation their place is taken by true yeasts. The terms wild yeast and true yeast as used by these authorities are rather confusing. I do not believe the yeasts alone account for the changes cacao undergoes when it ferments, and the above results corroborate my belief. The yeast used for inoculation was the yeast found growing on the cacao; consequently no error could have arisen from a choice of the wrong yeast.

For purposes of comparison and control, *C–6–TD, C–6–TD–S, C–6–y–S, F–6–TD, F–6–TD–S,* and *F–6–y–S* were run. These were no better than, and in some cases not so good as, *C–6–y* and *F–6–y*; therefore they add weight to the above conclusion that yeast is not solely responsible for the fermentation changes of cacao.

To determine, if possible, the influence of the enzymes on the cacao, samples *C–7–C, C–7–T, C–7–A, F–7–C, F–7–T,* and *F–7–A* were prepared. Extreme care was taken to prevent inoculation of the seeds when the pods were opened and the

[14] Loc. cit. [15] Loc. cit.

seeds removed. In this endeavor I was successful, since at no time was any alcoholic or acetic acid fermentation apparent. These samples were examined in the same manner as the preceding. The quality of the cacao was better than that produced by the action of yeast and taka-diastase in the absence of the enzymes, but the odor was not so fine as *C–6* in the case of the criollo samples so treated, nor so fine as *F–6* in the case of the forastero samples. Judging by these results, it would appear that the enzymes already existing in the cacao alone do not bring about all the desired changes, but that their influence must be reënforced by the enzymes from yeasts and possibly from bacteria or molds. The superiority or the peculiarity of certain cacaos is probably largely due to the presence of certain yeasts or molds during the fermentation process. It is instructive to cite the belief of Preyer [16] in this regard. He has isolated a yeast, *Saccharomyces theobromae,* from fermenting cacao. He recommends its use in the initiation of the fermenting process. The use of a pure culture yeast would necessitate extreme care in handling to prevent inoculation of the cacao with wild yeasts until the yeasts used for inoculation had attained a good growth. It would be impossible to sterilize the seeds, since such treatment would likewise destroy the enzymes, and the resulting product from enzyme-free cacao would not be satisfactory. The seeds as they exist in the pod are free from yeasts and bacteria, but handling of this in such a manner as to prevent contamination is hardly practical. However, care in fermentation will yield a good grade of material provided the initial product is high class, so there is no cause for disconsolation because of the apparent impracticability of using pure cultures of yeast.

## SUMMARY

Philippine cacao is compared with foreign cacaos.

A study is made of criollo and forastero cacao fermented under varying lengths of time, and the respective influence of the enzymes and of yeast is investigated.

The conclusion is reached that the Philippine Islands can grow a good quality of cacao in large quantities and that the time seems opportune for such an innovation. The investigation leads to the belief that the fermentation is the joint result of the reaction of yeasts and of enzymes.

[16] Preyer, A., *Tropenpflanzer* (1901), 5, 157.

# THE INTERACTION OF CHLORIDE OF LIME WITH THE NORMAL CONSTITUENTS OF NATURAL WATERS AND SEWAGE[1]

By GEORGE W. HEISE

FIVE TEXT FIGURES

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In the course of an extensive study of the sterilization of water and sewage, parts of which have already been reported, (9) it became necessary to do considerable work on the decomposition of chloride of lime (calcium hypochlorite) in water and on its interaction with waters and sewage. The work was done because of its practical importance, and no attempt was made to study in detail the chemical reactions involved; the results are presented at this time because of their possible application to sterilization problems involving the use of hypochlorite solutions.

The value of chloride of lime as a disinfectant was first pointed out by Koch (12) in 1881, while its application on a large scale to the sterilization of water for municipal supply was first proposed in 1894 by Traube. (23) That waters containing hydrogen sulphide or relatively large quantities of organic matter are not readily sterilized with chloride of lime was shown by Lode (14) in 1895. Since that time hypochlorites have been so widely used for the disinfection of water and sewage that their decomposition and their interaction with the substances normally found in water and sewage have been much studied.

Hypochlorites in distilled-water solution decompose, even in the dark, with measurable velocity. (2) Both chlorate and oxygen are formed, although the main reaction proceeds according to the equation

$$2NaClO \rightarrow 2NaCl + O_2.$$

The decomposition is accelerated by heat, proceeding in accordance with the equation: (2)

$$3NaClO \rightarrow NaClO_3 + 2NaCl, \text{ and}$$
$$2NaClO \rightarrow 2NaCl + O_2.$$

The results of Bhaduri (2) indicate that for certain concentrations in the dark at 100° C. the reaction is monomolecular,

[1] Received for publication December 1, 1916.

although its order has not been determined experimentally. The photolysis has been studied quantitatively by Lewis,(13) who concluded that the reaction was probably monomolecular.

When waters contain foreign substances either in solution or in suspension, the decomposition rate of hypochlorites is generally markedly changed. Bhaduri(2) found that in the dark a sodium hypochlorite solution was most stable when the concentration of sodium hypochlorite was 1.5–1.7 per cent; of salt molecules, approximately 0.4 per cent. In the light,(13) alkaline is more stable than neutral sodium hypochlorite solution. Concentration and temperature have very little effect(6) on the stability. Elements of the iron group accelerate decomposition; the presence of magnesium and aluminium increases the instability when the alkalinity is low. Elmanowitsch and Zaleski(4) found that acids increased, while alkalies decreased, the amount of (calcium) hypochlorite decomposed (at boiling temperature) by natural waters. Such factors as temperature, alkalinity, and the presence of phenols and hydrogen sulphide promote the decomposition of hypochlorites in sewage.(5)

The accelerating influence of a high organic content in water on the decomposition of hypochlorites has been much studied. Asparagin, peptone and allied products,(8) albumin and its decomposition products,(4) sewage,(5) urine, sweat, saliva, and body products in general(10) have an especially great effect on the chlorine consumption. Apparently there is no direct parallelism between oxygen-consuming capacity (as measured by the reduction of permanganate solution) and chlorine-consuming power,(14) this no doubt due partly to the well-known inaccuracy of determinations of oxygen-consuming capacity in regard to both quantity and kind of organic matter present in water, partly to specific interaction between the substances in water with chlorine.

At first the disappearance of available chlorine from chlorinated water or sewage is very rapid, but it soon becomes slow. The reaction proceeds as though there were present, in some waters at least, substances which are so readily oxidized by chlorine that they take it up before it can destroy the bacteria present. Although the bactericidal action of chlorine occurs simultaneously with the chemical decomposition, the latter might proceed rapidly enough greatly to impede or even to nullify the former. After the chlorine is once destroyed, bacterial growth might proceed unchecked, which furnishes a possible explanation for the repeatedly noted phenomenon—the great increase

in bacterial content of waters in municipal distribution systems at varying periods after chlorination.(15)

Much work remains to be done on the substances formed by the interaction of hypochlorites with the organic matter found in water. It is because of these substitution products(16, 20) that chlorinated waters used for public supplies often retain a peculiar chlorine odor and taste after all chemical trace of free chlorine has disappeared. In such cases—(21)

> these tastes and odours are not occasioned so much by chlorine or hypochlorites themselves as by inorganic and organic chloramines, and possibly other chlorine-substituted compounds formed by interaction with the organic matters present in waters. * * * They [the chloramines] are all germicidal, and all possess a more or less disagreeable odour. * * * He [Rideal] proved that chlorine * * * was working by substitution for hydrogen in ammonia and organic compounds, yielding products [chloramine and hydrazine] of higher germicidal power than chlorine itself.

Race(19) found that when ammonia was added to hypochlorites, in the proportion of 1 part ammonia to 2 parts of available chlorine, the germicidal action was increased threefold.

While the addition of alum causes an immediate reduction in available chlorine, it has no apparent effect on the bactericidal properties of the solution for twelve hours, according to the findings of Avery and Lye.(1)

With waters high in organic matter it is probable that the main chemical change follows the course of a monomolecular reaction as in the case in the decomposition of hypochlorites in distilled water. However, there are, apparently, so many simultaneous reactions that the accurate determination of the velocity constant is not easy. From the fact that, in general, the amount of chlorine consumed by sewage in a given time is proportional to the amount of chlorine added, Glaser(5) concluded that the reaction is monomolecular. Race(18) followed the course of the reaction between hypochlorites and a colored water and came to the same conclusion.

The effect of light, though a most important factor in the decomposition rate of hypochlorites, has been frequently overlooked or at least insufficiently emphasized, so that some of the work which has been done is not conclusive. The importance of this factor in the sterilization of swimming pools has already been discussed.(10)

## EXPERIMENTAL PART

*Determination of available chlorine.*—For the work recorded in this paper, chlorine was quantitatively determined in the

usual manner by titration with standard sodium thiosulphate solution in the presence of phosphoric acid, potassium iodide, and starch solutions, care being taken to keep such factors as temperature and concentration as uniform as possible to ensure comparable results. Phosphoric acid was used instead of hydrochloric or sulphuric acid, because errors in titration due to the presence of ferric iron and chlorates are thus avoided. (11) The following graduation (4) of this determination, on the basis of the color of the iodine-starch reaction in the presence of hydrochloric acid, serves very well for the estimation of very small quantities of chlorine in 200 cubic centimeter samples:

Doubtful, when Cl content is 0.11 mg. per liter.
Barely noticeable, when Cl content is 0.12 mg. per liter.
Noticeable, when Cl content is 0.13 mg. per liter.
Weak, when Cl content is 0.17 mg. per liter.
Distinct, when Cl content is 0.24 mg. per liter.
Sharp, when Cl content is 0.4 mg. per liter.

*The decomposition rate of calcium hypoclorite solution in the dark.*—In order to study the decomposition rate of hypochlorites, known quantities of standard filtered chloride of lime solution were added to water in large glass jars provided with ground glass covers. Aliquot portions were pipetted off from time to time and analyzed.

Whether the reaction was followed in distilled water, natural (artesian or river) waters, in solutions of organic substances, or in sewage, the decomposition curve had the same general trend. At first there was a rapid disappearance of chlorine, followed by an abrupt slowing down of the reaction. This sudden change of velocity generally occurred within from thirty minutes to one hour, after which the reaction proceeded very slowly, but very regularly, showing no sign of reaching an end point, though followed for weeks. Therefore it appears probable that the main reaction between chloride of lime and dissolved substances quickly approaches completion, after which the curve of gradual decomposition in water is followed. The experimental data secured are shown in Table I. The results for sewage were the most striking, and as they are apparently typical, on a large scale, of the reactions occurring in the other liquids, they are shown graphically in fig. 1.

For the sake of completeness, the data for distilled water are plotted in fig. 2 for the entire eight hundred ninety hours during which the reaction was under observation. The curve appears to be typical for all of the reactions in the table. Though the

reaction was carried on in a small dark room the daily temperature variation of which was probably less than 3° C., the temperature change no doubt affected the results somewhat. Experimental errors appear somewhat exaggerated on the curve, because of the large scale on which chlorine concentrations are

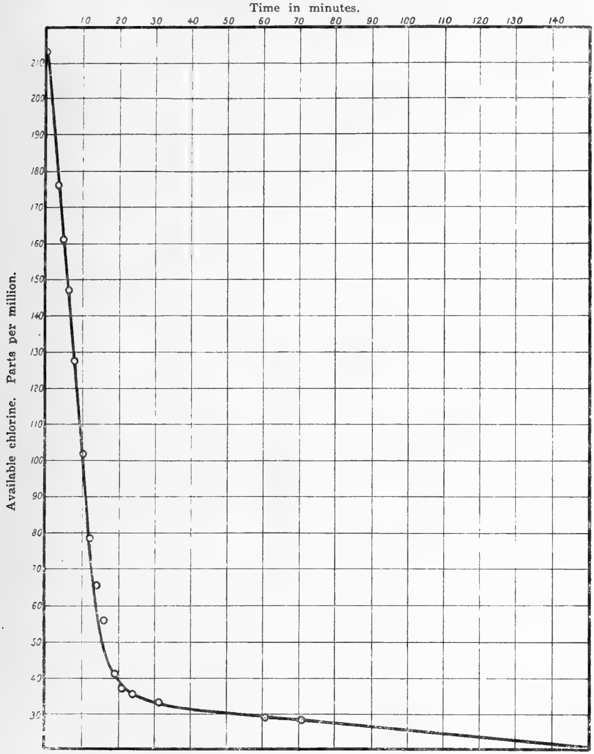


**Fig. 1. The decomposition of chloride of lime in sewage in the dark.**

shown. The abrupt change in velocity indicated in fig. 1 does not appear in fig. 2, owing to the small scale on which time is plotted in the latter.

TABLE I.—*Decomposition of chloride of lime in the dark.*[a]

IN DISTILLED WATER.

| Time. | | Available chlorine. Parts per million. |
|---|---|---|
| *Hrs.* | *mins.* | |
| 0 | 0 | [b]37.2 |
| 0 | 6 | 36.0 |
| 0 | 11 | 35.5 |
| 0 | 15 | 35.1 |
| 1 | 14 | 34.8 |
| 5 | 43 | 34.4 |
| 23 | 34 | 33.1 |
| 29 | 15 | 33.0 |
| 48 | 0 | 32.5 |
| 70 | 0 | 31.0 |
| 98 | 0 | 30.6 |
| 194 | 0 | 29.6 |
| 890 | 0 | 26.6 |

IN ARTESIAN WELL WATER.

| Time. | | Available chlorine. Parts per million. |
|---|---|---|
| 0 | 0 | [b]38.4 |
| 0 | 4 | 37.9 |
| 0 | 10 | 34.2 |
| 0 | 16 | 34.2 |
| 0 | 54 | 33.9 |
| 5 | 0 | 33.5 |
| 23 | 0 | 32.7 |
| 30 | 0 | 32.4 |
| 54 | 0 | 31.5 |
| 70 | 0 | 31.0 |

IN 5 LITERS DISTILLED WATER PLUS 0.1 GRAM AMMONIUM ACETATE.

| Time. | | Available chlorine. Parts per million. |
|---|---|---|
| *Hrs.* | *mins.* | |
| 0 | 0 | [b]36.0 |
| 0 | 6 | 35.0 |
| 0 | 12 | 34.2 |
| 0 | 32 | 30.8 |
| 0 | 37 | 30.7 |
| 3 | 30 | 5.00 |
| 5 | 0 | 4.75 |
| 5 | 35 | 4.47 |
| 22 | 0 | 3.78 |
| 46 | 0 | 3.15 |
| 73 | 0 | 2.8 |
| 145 | 0 | 2.1 |

IN 0.001 MOLAR OXALIC ACID.[c]

| Time. | | Available chlorine. Parts per million. |
|---|---|---|
| 0 | 0 | [b]37.0 |
| 0 | 4 | 9.6 |
| 0 | 9 | 4.5 |
| 0 | 17 | 2.7 |
| 0 | 55 | 2.4 |
| 3 | 46 | 1.9 |
| 3 | 51 | 2.0 |
| 23 | 0 | 1.4 |

IN SEWAGE.

| Time. | | Available chlorine. Parts per million. |
|---|---|---|
| *Hrs.* | *mins.* | |
| 0 | 0 | [b]228.0 |
| 0 | 2 | 116.0 |
| 0 | 6 | 100.0(?) |
| 0 | 9 | 38.0 |
| 0 | 15 | 35.2 |
| 0 | 49 | 30.5 |
| 21 | 20 | 22.0 |
| 45 | 0 | 14.5 |
| 0 | 0 | 213.0 |
| 0 | 2 | 190.0 |
| 0 | 4 | 176.0 |
| 0 | 5 | 161.0 |
| 0 | 7 | 147.0 |
| 0 | 8 | 127.5 |
| 0 | 11 | 102.0 |
| 0 | 13 | 78.6 |
| 0 | 15 | 65.5 |
| 0 | 17 | 55.8 |
| 0 | 20 | 41.2 |
| 0 | 22 | 37.2 |
| 0 | 25 | 35.5 |
| 0 | 28 | 35.4 |
| 0 | 32 | 33.3 |
| 1 | 1 | 29.4 |
| 1 | 11 | 28.7 |
| 2 | 29 | 20.7 |

[a] In this and subsequent tables some of the experimental results were verified by R. H. Aguilar, chemist, Bureau of Science.

[b] Calculated.

[c] The decomposition of hypochlorite proceeded so rapidly in 0.1 molar oxalic acid solution that it could not be followed quantitatively.

TABLE II.—*Decomposition of a solution of chloride of lime in tap water in diffused daylight.*

| Time. | | Available chlorine. Parts per million. | Time. | | Available chlorine. Parts per million. |
|---|---|---|---|---|---|
| *Hrs.* | *mins.* | | *Hrs.* | *mins.* | |
| | 0 | 0.8 | | 0 | 10.0 |
| | 2 | 0.6 | | 2 | 9.7 |
| | 30 | 0.3 | | 45 | 8.5 |
| 2 | 00 | trace | 1 | 25 | 7.9 |
| | | | 3 | 45 | 7.0 |

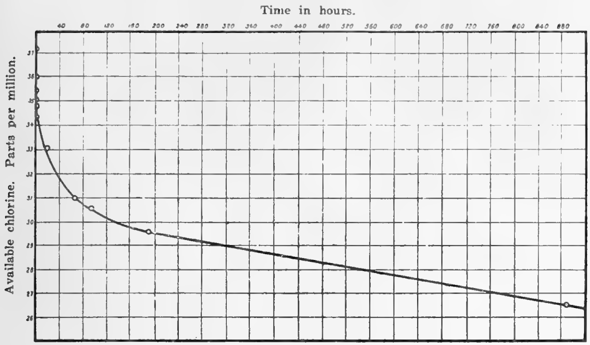

FIG. 2. The decomposition of chloride of lime in distilled water in the dark.

The data at hand for the progressive decomposition of chloride of lime do not show clearly the order of reaction. The decomposition in sewage is probably a heterogeneous reaction.(17) Fig. 1 shows that for a time the reaction velocity was practically constant $\left(\frac{dx}{dt}=K; K=\frac{x}{t}\right)$.

*The decomposition rate of calcium hypochlorite solution in the light.*—In the light the decomposition more nearly approached the typical rate of a monomolecular reaction. The data obtained in a typical series of determinations are given in Table II and are plotted in fig. 3. Comparison with fig. 1 shows clearly the difference between the course of the dark and the light reaction. As indicated in the curve, the photochemical decomposition proceeded in a regular manner. As the experiments were performed in the diffused light of the laboratory, the light was a variable factor and caused deviations from the true course of the photochemical decomposition.

It is interesting to note in this connection that in measurements of the decomposition of chloride of lime in different waters in the dark and in the light the differences between the amounts decomposed in the light and in the dark were very uniform for any given light intensity, regardless, within the limits observed, of the specific chlorine-binding power of the various waters used. This is evident from the data in Table III. The last column shows that for any one day the differences between the "light" and "dark" determinations were nearly the same, though the waters under observation varied widely in their ability to decompose chloride of lime in the dark.

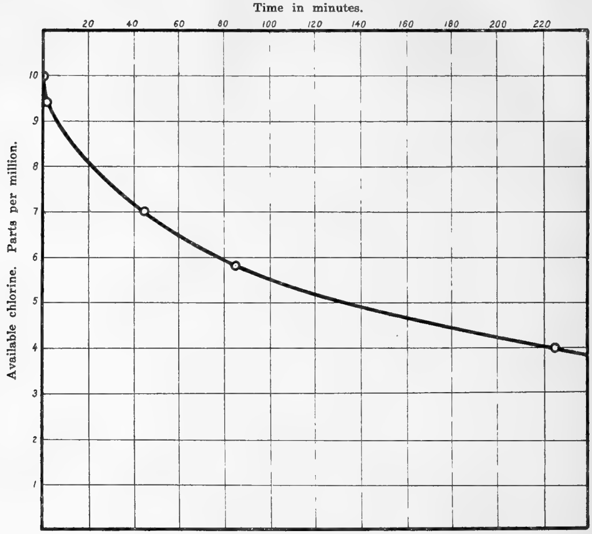


FIG. 3. The decomposition of chloride of lime solution in diffused daylight.

TABLE III.—*Effect of light on chlorine consumption; 200 cubic centimeter samples of different waters digested two hours at 28°C.*

| Day. | Sample. | Available chlorine added. | Available chlorine consumed. In diffused daylight. | Available chlorine consumed. In dark. | Difference. |
|---|---|---|---|---|---|
| | | *mg.* | *mg.* | *mg.* | *mg.* |
| 1 | A | 2.9 | 0.28 | 0.11 | 0.17 |
| | B | 2.9 | 0.47 | 0.25 | 0.22 |
| [a]2 | C | 2.9 | 0.14 | 0.14 | 0.00 |
| | D | 2.9 | 0.45 | 0.45 | 0.00 |
| 3 | E | 2.7 | 0.50 | 0.24 | 0.26 |
| | F | 2.7 | 0.66 | 0.45 | 0.21 |
| 4 | G | 2.7 | 0.65 | 0.23 | 0.42 |
| | H | 2.7 | 0.87 | 0.43 | 0.44 |
| 5 | I | 2.7 | 0.53 | 0.23 | 0.30 |
| | J | 2.7 | 0.60 | 0.28 | 0.32 |

[a] Sky was heavily overcast, and laboratory was dark.

*The interaction of chloride of lime and organic matter as affected by concentration.*—If the interaction of chloride of lime with organic matter is a monomolecular reaction, it follows directly that the percentage of chloride of lime decomposed should be independent of the initial concentration. In other words, the amount of chlorine consumed in a given time should be a constant fraction of the quantity added. For example, (5) when the addition of available chlorine to sewage is doubled, the amount of chlorine absorbed will also be doubled, within certain limits, a fact which has an important bearing on the economical application of hypochlorites for disinfecting purposes.

A good illustration of this regularity is shown in the following series of determinations on the interaction of chloride of lime and urea. Different quantities of filtered chloride of lime solution, varying in strength from 2 to about 100 milligrams of available chlorine, were diluted to 100 cubic centimeters, placed in glass-stoppered bottles, and digested twenty-one hours in the dark at 28° C. with 2 cubic centimeters of 0.01 molar urea solution. At the end of the digestion period the samples were analyzed, with the results listed in Table IV.

TABLE IV.—*Interaction of varying concentrations of calcium hypochlorite with urea.*

| Hypochlorite added as— | | Available chlorine consumed. | |
|---|---|---|---|
| Solution. | Available chlorine. | Observed. | Calculated.[a] |
| *cc.* | *mg.* | *mg.* | *mg.* |
| 1.0 | 2.3 | 2.1 | 2.2 |
| 1.5 | 3.4 | 3.1 | 3.3 |
| 2.0 | 4.6 | 4.3 | 4.4 |
| 3.0 | 6.9 | 6.5 | 6.6 |
| 4.0 | 9.2 | 8.8 | 8.9 |
| 5.0 | 11.5 | 11.0 | 11.1 |
| 6.0 | 13.8 | 13.3 | 13.3 |
| 7.0 | 15.3 | 14.9 | 15.5 |
| 8.0 | 18.3 | 17.7 | 17.7 |
| 9.0 | 20.6 | 20.0 | 20.0 |
| 10 | 22.9 | 22.2 | 22.2 |
| 15 | 34.4 | 33.5 | 33.3 |
| 20 | 45.8 | 44.5 | 44.4 |
| 25 | 57.2 | 55.6 | 55.5 |
| 30 | 68.7 | 67.0 | 66.6 |
| 40 | 91.6 | 83.7 | 88.8 |

[a] From the values obtained with 6, 8, 9, and 10 cubic centimeters of solution.

Almost without exception the experimental results vary from the calculated values by quantities well within the range of experimental error. Apparently this regularity holds good for wide ranges of concentration with many different substances.[2] Even with fairly pure natural waters similar results may be obtained under certain conditions. Thus 100 cubic centimeter samples of a clear river water, boiled with varying amounts of filtered chloride of lime solution for fifteen minutes in diffused daylight, reacted as follows:

TABLE V.—*The interaction of a river water and varying quantities of chloride of lime solution at 100°C.*

| Chloride of lime added as— | | Chloride of lime consumed as— |
|---|---|---|
| Solution. | Available chlorine. | Available chlorine. |
| *cc.* | *mg.* | *mg.* |
| 1 | 3.36 | 0.52<br>0.49 |
| 2 | 6.72 | 0.96<br>0.84 |
| 3 | 10.1 | 1.68<br>1.82 |

The ratio of the amounts of chlorine consumed is approximately the same as that of the amounts added, namely, 1 : 2 : 3.

With sewage there is a similarity of reaction, with some curious differences. The percentage of chlorine consumed may increase with increasing additions of chloride of lime, giving rise to the peculiar phenomenon that the available chlorine left is greater after digestion with small quantities of chloride of lime than after digestion with much larger quantities for an equal period of time. This observation was repeated too frequently to be capable of explanation on the ground of experimental error, though some series showed these abnormalities to a lesser degree than others.

This irregularity in chlorine consumption is also evident in the data of previously published work. For example, Glaser (5) says in effect:

As a matter of fact, there are at hand several experiments which deviate from the regular order, for instance, the progressive decomposition with

[2] Avery and Lye (1) found that upon the addition of alum to water the available chlorine was apparently reduced, within certain limits, in direct proportion to the amount of alum added.

a concentration of chloride of lime of 1:1000 recorded in tables 28 and 29 * * * [but] * * * a similar marked decrease in available chlorine could not be detected on repeating the experiments with the same concentration. It should be pointed out that there are other small deviations from the theoretical quantities of chlorine.

The analytical data given in Table VI show clearly that at certain concentrations the reaction is completely changed and that the irregularities noted by Glaser were not due to experimental error.

TABLE VI.—*Decomposition of chloride of lime in fresh sewage*[a] *(concentration of chloride of lime expressed as milligrams of available chlorine).*

A. EFFECT WITH VARYING PERIODS OF DIGESTION.

| Series 1.[b] | | | Series 2.[c] | | Series 3.[d] | | Series 4.[d] | | |
|---|---|---|---|---|---|---|---|---|---|
| Added. | Left. | Consumed. | Left. | Consumed. | Left. | Consumed. | Added. | Left. | Consumed. |
| 4.69 | 3.55 | 1.14 | 3.61 | 1.08 | 2.93 | 1.76 | 1.17 | 0.5 | 0.7 |
| | 3.45 | 1.24 | 1.34 | 3.35 | 2.76 | 1.93 | 2.34 | 1.3 | 1.0 |
| | 3.32 | 1.37 | 1.30 | 3.39 | 2.82 | 1.87 | 4.69 | 2.9 | 1.8 |
| 9.38 | 0.50 | 8.88 | 0.85 | 8.53 | 0.48 | 8.90 | 7.03 | 4.4 | 2.6 |
| | 0.58 | 8.80 | 1.08 | 8.30 | 0.78 | 8.60 | 9.38 | 2.0 | 7.4 |
| | 0.53 | 8.85 | 1.32 | 8.06 | 0.38 | 9.00 | 11.71 | 1.2 | 10.5 |
| 18.75 | 7.40 | 11.35 | 5.80 | 12.95 | 4.11 | 14.64 | 14.09 | 0.5 | 13.6 |
| | 7.17 | 11.58 | 5.55 | 13.20 | 3.55 | 15.20 | 16.43 | 0.8 | 15.6 |
| | 7.24 | 11.51 | 5.50 | 13.25 | 4.03 | 14.72 | 18.75 | 1.3 | 17.4 |
| | | | | | | | 21.1 | 3.0 | 18.1 |
| | | | | | | | 23.4 | 4.3 | 19.1 |
| | | | | | | | 25.8 | 5.6 | 20.2 |
| | | | | | | | 28.1 | 7.5 | 20.6 |
| | | | | | | | 37.5 | 15.8 | 21.7 |

[a] Sewage, 50 cubic centimeters; temperature of digestion, 28° C.
[b] Time of digestion, forty-five minutes.
[c] Time of digestion, one hundred minutes.
[d] Time of digestion, eighteen hours.

B. EFFECT WITH SEWAGE SAMPLES OF DIFFERENT AGES.

| Series 5. Fresh sewage. | | | | Series 6. Same sample, after 24 hours. | | | |
|---|---|---|---|---|---|---|---|
| Added. | Left. | Consumed. | | Added. | Left. | Consumed. | |
| | | | *Per cent.* | | | | *Per cent.* |
| 1.10 | 0.07 | 1.03 | 94 | 1.00 | 0 | 1.00 | 100 |
| 2.20 | 0.47 | 1.73 | 79 | 2.00 | 0.26 | 1.74 | 87 |
| 4.40 | 0.95 | 3.45 | 79 | 3.00 | 0.42 | 2.58 | 86 |
| 8.80 | 0.24 | 8.56 | 97 | 4.00 | 0.64 | 3.36 | 84 |
| 17.6 | 1.7 | 15.9 | 90 | 5.00 | 1.10 | 3.90 | 78 |
| 35.2 | 15.8 | 19.4 | 55 | 6.00 | 1.20 | 4.80 | 80 |
| 70.4 | 47.8 | 22.6 | 32 | 7.00 | 1.90 | 5.10 | 73 |
| | | | | 8.00 | 1.35 | 6.65 | 83 |
| | | | | 10.0 | 1.00 | 9.00 | 90 |
| | | | | 30.0 | 15.8 | 14.2 | 47 |
| | | | | 40.0 | 25.2 | 14.8 | 37 |
| | | | | 50.0 | 33.5 | 16.5 | 33 |

TABLE VI.—*Decomposition of chloride of lime in fresh sewage (concentration of chloride of lime expressed as milligrams of available chlorine)*—Continued.

C. EFFECT WITH CONSTANT VOLUME OF LIQUID (CONCENTRATIONS OF CHLORIDE OF LIME EXPRESSED AS PARTS PER MILLION OF AVAILABLE CHLORINE).

| Series 7. | | | | Series 8. | | |
|---|---|---|---|---|---|---|
| Added. | Left. | Consumed. | | Left. | Consumed. | |
| | | | *Per cent.* | | | *Per cent.* |
| 4.6 | 1.9 | 2.7 | 59 | 0.6 | 4.0 | 87 |
| 9.2 | 3.7 | 5.5 | 60 | 3.2 | 6.0 | 65 |
| 18.4 | 7.3 | 11.1 | 60 | 10.6 | 7.8 | 42 |
| 27.5 | 13.7 | 13.8 | 50 | 18.1 | 9.4 | 34 |
| 45.8 | 16.4 | 29.4 | 64 | 28.0 | 17.8 | 39 |
| 64.2 | 5.2 | 59.0 | 92 | 27.5 | 36.7 | 57 |
| 82.5 | 3.5 | 79.0 | 96 | 8.5 | 74.0 | 90 |
| 110 | 6.0 | 154 | 94 | 4.0 | 106 | 96 |
| 138 | 13.0 | 125 | 91 | 6.0 | 132 | 95 |
| 184 | 41.0 | 143 | 78 | 21.0 | 163 | 88 |
| 275 | 108 | 167 | 61 | 91.0 | 184 | 67 |
| 368 | 197 | 171 | 47 | 171 | 197 | 54 |
| 460 | 249 | 211 | 46 | 258 | 202 | 44 |
| 690 | 445 | 245 | 36 | 472 | 218 | 32 |
| 920 | 707 | 213 | 23 | 690 | 230 | 25 |
| 1,835 | 1,385 | 450 | 25 | 1,415 | 420 | 23 |
| 2,750 | 2,093 | 657 | 24 | 1,925 | 825(?) | 30 |
| 4,580 | 3,615 | 965 | 21 | 3,330 | 1,250(?) | 27 |

The foregoing data show the peculiar fact that with increasing additions of available chlorine the amount left after digestion first increased, next decreased, and finally again increased. For certain concentrations the available chlorine left after digestion was greater with small additions of chlorine than with much larger ones. The different series listed above were obtained on different days with different samples of sewage, so that the agreement between the results recorded is as good as is to be expected. As a matter of fact, different samples vary greatly and the same samples change with time, as indicated by the differences between series 6 and series 7.

Owing to the change in the volume of the digested liquid, caused by large additions of chloride of lime solutions, discrepancies in the analytical results may occur. In series 8 these deviations were avoided by keeping the quantity of liquid constant by the addition of enough water to the first members of the series to compensate for the differences in volume caused by the addition of chloride of lime solution.

Typical series in the foregoing table are graphically shown in

fig. 4, the experimental data from Glaser's (5) Table XXIX for 20-hour digestion periods being inserted for comparison. For use in this figure, the data in Table VI were recalculated as parts per million.

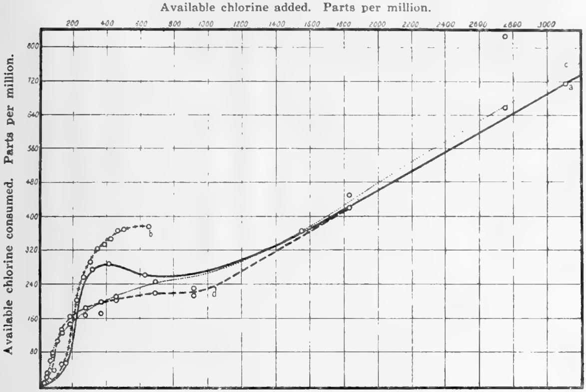


FIG. 4. The decomposition of chloride of lime in sewage in the dark. *Curve a*, results of Glaser; *curve b*, Table VI, series 4; *curve c*, Table VI, series 7; *curve d*, Table VI, series 8.

*Effect of the concentration of substances reacting with chloride of lime.*—The more concentrated the solution with which the chloride of lime reacts, the more chlorine is used up. This is to be expected, and it has been pointed out so often that it needs no further proof here. There is, however, a curious anomaly which may occur and which may lead to confusion in the interpretation of the ordinary laboratory tests of the chlorine-binding power of a water. The interaction of urea and chloride of lime in the dark at moderate temperature furnishes an illustration of this, when the decomposition of chloride of lime is measured in the usual manner, that is, by means of standard sodium thiosulphate, in the presence of potassium iodide, phosphoric acid, and starch.

In Table VII are the results obtained when the same quantity of chloride of lime was allowed to react with different quantities of urea. They show that, for very low concentrations of urea, increase in concentration leads to increased chlorine consumption; with higher concentrations, however, the chlorine con-

sumption decreases. The results are also shown graphically in fig. 5.

The scope of the work does not warrant a detailed study of this reaction [3] at this time. The results are presented because they are sufficiently definite to show the disturbing factors that may be present in the tests of the chlorine consumption of a water or sewage. Probably different chlorine-substitution products are formed with different concentrations of urea, some of which react immediately with potassium iodide, liberating iodine, some reacting slowly or not at all, so that the amount of

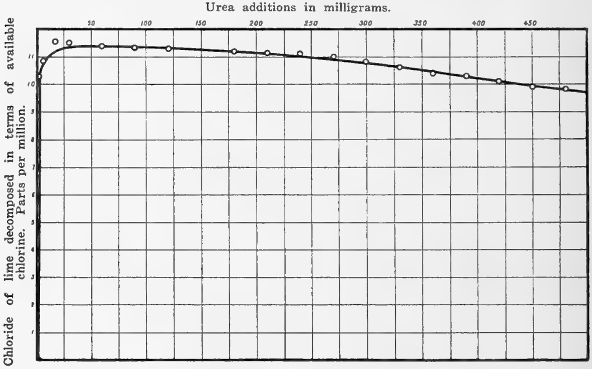


FIG. 5. The decomposition of chloride of lime in urea solutions of varying concentrations in the dark.

available chlorine left in solution may not be a true measure of the reaction. Since these products may have even stronger disinfecting action (21) than chloride of lime, the determination of chlorine consumed is not necessarily an index of the quantity of hypochlorite required for disinfection.

According to Hairi, (8) the liquids in which the disinfecting action of chlorine is greatly retarded show a strong chlorine-consuming power. In a solution of peptone, for example, neither the chlorine consumption nor the inhibition of germicidal action varies in the same manner as the concentration.

[3] After this work had been completed, I found that Dakin (3) had reported a similar anomalous reaction between hypochlorous acid and sheep serum.

TABLE VII.—*Interaction of chloride of lime solution with varying concentrations of urea.*

[Water, 100 cubic centimeters; urea, additions as noted. Five cubic centimeters of chloride of lime solution digested eighteen hours in the dark at 28°C.]

SERIES A. ADDITION—11.0 MILLIGRAMS AVAILABLE CHLORINE.

| Urea. | | Available chlorine. | |
|---|---|---|---|
| Solution added. | Weight added. | Consumed. | Left. |
| *cc.* | *g.* | *mg.* | *mg.* |
| 0 | 0 | 0.05 | 10.9 (5) |
| 0.1 | 0.003 | 10.3 | 0.7 |
| 0.25 | 0.007 | 10.8 (6) | 0.1 (4) |
| 0.50 | 0.015 | 10.8 (4) | 0.1 (6) |
| 1.00 | 0.030 | 10.8 | 0.2 |

SERIES B. ADDITION—11.8 MILLIGRAMS AVAILABLE CHLORINE.

| | | | |
|---|---|---|---|
| 0 | 0 | 0.1 | 11.7 |
| 0.5 | 0.01 (5) | 11.5 (5) | 0.1 (5) |
| 1.0 | 0.03 | 11.5 | 0.3 |
| 2.0 | 0.06 | 11.4 | 0.4 |
| 3.0 | 0.09 | 11.3 (5) | 0.4 (5) |
| 4.0 | 0.12 | 11.3 | 0.5 |
| 6.0 | 0.18 | 11.2 | 0.6 |
| 7.0 | 0.21 | 11.1 (5) | 0.6 (5) |
| 8.0 | 0.24 | 11.1 | 0.7 |
| 9.0 | 0.27 | 11.0 | 0.8 |
| 10.0 | 0.30 | 10.8 | 1.0 |
| 11.0 | 0.33 | 10.6 (5) | 1.1 (5) |
| 12.0 | 0.36 | 10.4 | 1.4 |
| 13.0 | 0.39 | 10.3 | 1.5 |
| 14.0 | 0.42 | 10.1 | 1.7 |
| 15.0 | 0.45 | 9.9 | 1.9 |
| 16.0 | 0.48 | 9.8 | 2.0 |

## GENERAL DISCUSSION

Since there is no direct parallelism between the oxygen-consuming capacity and the amount of chlorine a water or sewage is capable of taking up, the determination of chlorine-consuming capacity, in spite of its limitations, is an important test in the laboratory control of hypochlorite disinfection. Hairi (8) digested 100 cubic centimeter samples with chloride of lime solution in excess (13 milligrams available chlorine) and titrated after an hour in weakly acid solution. If digestion is carried out at constant temperature in the dark, this procedure will give concordant, relative values for the chlorine absorption.

Elmanowitsch and Zaleski (4) recommended the determination

of chlorine consumption at boiling temperature, with carefully regulated constant heating, for fifteen-minute digestion periods, with lime water added to the water under examination. The authors obtained very concordant results by this process. The figures given in Table V were obtained without addition of lime water, but show that the method is accurate enough for laboratory use. However, this method is open to objection, because it does not take into account conversion of hypochlorite to chlorate at boiling temperature.

Digestion in the dark at room temperature is so easily carried out, and gives such uniform results if care is used in keeping conditions constant, that it is to be preferred to the methods employing heat.

Whether chloride of lime shows fluctuations in bactericidal effect similar to those noted for its chemical decomposition (Table VI, fig. 4) is not clear. The results of Glaser(5) indicate that it does not, but these observations were made with such high concentrations of chloride of lime that they are not conclusive.

It is true that the data under discussion were obtained in experiments on sewage, but apparently similar fluctuations may occur with ordinary water as well and with small hypochlorite concentration. Thus Stokes and Hachtel(22) in their work on the treatment of Baltimore spring water by calcium hypochlorite report that—

> when 1.5 parts of available chlorine per million parts of water were used there is practically no residual chlorine in the water. In one case when 1.75 parts were used there was a large amount of residual chlorine, giving an average . . . . of .574. On another occasion, however, when this amount was used the residual chlorine was less, giving an average of 0.24 per million parts of water. When 2.0 parts of available chlorine were used there was an average . . . of 0.206, and when 2.5 parts of available chlorine were used for treatment there was an average of 0.62 parts per million parts of water. These results, therefore, are somewhat variable, and it is hard to explain the greater amount of residual chlorine when 1.75 parts were used than when 2.0 parts were used.

From the evidence at hand it is clear that the ordinary procedures for determining the amount of interaction between hypochlorites and waters and sewage are influenced by so many factors that, unless very carefully interpreted, they are very likely to be misleading. If it were only the available chlorine that had germicidal action, the analytical control of hypochlorite sterilization would be relatively simple. Even in this case, however, the quality of a water would be an important consideration, since waters differ widely in their ability to liberate chlorine from hypochlorites.(21) Thus two different waters brought to

this laboratory were treated with chloride of lime solution and immediately titrated with sodium thiosulphate in the usual manner. Acidified, 100 cubic centimeter samples showed 6.5 milligrams of available chlorine, whereas unacidified samples showed only 2.4 and 4.0 milligrams, respectively. Since the amount of chlorine taken up by water or sewage depends upon the amount and concentration of chlorine added, on the temperature and time of digestion, on light, and on the quality of the liquid studied, it is obvious that, at best, only relative data, available for laboratory control of disinfection problems, are obtained by the methods ordinarily employed. Such determinations do not necessarily give any indication of the presence of germicidal products formed by the interaction of hypochlorites and the ingredients of waters and sewage; hence they lose much of their significance for disinfection problems unless they are studied in conjunction with bacteriological data. In all cases, the chlorine consumption should be determined as nearly as possible under the same conditions of temperature, illumination, and concentration that obtain in actual practice.

## SUMMARY

The decomposition rate of chloride of lime in water, sewage, and solutions of organic substances was studied. In the dark, at 28° C., the reactions proceeded with almost constant velocity for periods of thirty minutes to one hour, after which they proceeded very slowly. In the light the decomposition rate was greatly accelerated.

In general, the amount of available chlorine consumed is proportional to the concentration in which it is added, as shown by the interaction of chloride of lime and urea solution. However, for certain definite concentrations of sewage this regularity fails.

A study of the reaction between chloride of lime with varying quantities of urea showed that the chlorine consumption, as measured by the starch-potassium-iodide reaction, is not necessarily proportional to the concentration of organic matter.

The determination of the chlorine consumption of a water or sewage, though of importance in the control of hypochlorite disinfection, is not sufficient in itself and should be supplemented by bacteriological tests.

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# ILLUSTRATIONS

## TEXT FIGURES

# A CHEMICAL INVESTIGATION OF THE SEEDS OF PANGIUM EDULE AND OF HYDNOCARPUS ALCALÆ [1]

By Harvey C. Brill

*(From the Laboratory of Organic Chemistry, Bureau of Science, Manila)*

In an article [2] describing the investigation of the seeds of *Hydnocarpus venenata* and the properties of the oil from these seeds, announcement was made of the continuation of this investigation on the oils from seeds of various related plants growing in the Philippine Islands. The examination of such seeds was undertaken because of the fact that they are closely allied to the genus *Hydnocarpus,* which is closely related to the genus *Taraktogenos,* in order to determine if they have properties similar to the seeds of the latter. Chaulmoogra oil is obtained from *Taraktogenos,* but without doubt much of the oil sold as chaulmoogra is obtained from *Hydnocarpus,* since the chemical properties of certain of these oils are practically identical with the properties of chaulmoogra oil, which would make substitution easy and practically impossible to detect. Data concerning the seeds of *Pangium edule* Reinw. and *Hydnocarpus alcalæ* C. DC. are herewith presented.

## PANGIUM EDULE REINWARDT

*Pangium edule* is indigenous to the Malayan Archipelago and is found in various parts of the Philippine Islands. The seeds are flattened; their average size is about 5 centimeters long by 3 centimeters wide. They are embedded in a crustaceous pericarp, which is about 22 centimeters long by 15 centimeters in diameter. Mature and immature seeds were examined.

The *Pangium edule* seeds used by me were furnished by the Philippine Bureau of Forestry.

De Jong [3] announces the isolation of a cyanogenetic glucoside from the leaves of *Pangium edule* that is identical in all respects with that found in *Gynocardia odorata* by Power et. al.[4]

[1] Received for publication November, 1916.

[2] Brill, Harvey C., *This Journal, Sec. A* (1916), **11**, 75.

[3] De Jong, Awk., Recueil des travaux chimiques des Pays-Bas et de la Belgique (1909), **28**, 24; ibid. (1911), **30**, 220.

[4] Power, F. B., and Lees, F. H., *Journ. Chem. Soc. London* (1905), **87**, 349; Power, F. B., and Barrowcliff, M., ibid. (1905), **87**, 896.

and named gynocardin by them. As the glucoside is accompanied by an emulsinlike ènzyme, gynocardase, in the plant, any delay in working up the seeds or leaves entails a loss in the glucoside content, due to its hydrolysis by the enzyme. In order that this loss might be reduced to a minimum, instructions were given to the Bureau of Forestry rangers to heat the seeds in boiling water for one hour, insuring the destruction of the gynocardase, and then to dry them in the sun before delivery to the Bureau of Science. In spite of this precaution, in several cases an odor of hydrocyanic acid was noticeable when the seeds were received, showing that hydrolysis of the glucoside had taken place. These particular samples were not dry. Owing to the lateness of the rainy season and the prevalence of rain, it was impossible for them to be dried properly before shipment and they molded somewhat in transit. Dox[6] has shown that molds formulate all the known enzymes, regardless of the character of the substrase; consequently the small amount of glucoside present in some of the seeds received may have been due to the action of enzymes formed in this manner. As stated, both mature and immature seeds were received and examined. The mature seeds in no case gave any large amount of hydrocyanic acid when tested for the presence of gynocardin. The failure of strong positive tests cannot be attributed to the hydrolysis by molds in every case, since of the several samples of mature seeds examined not all were molded. It would appear that the amount of this glucoside decreases as the seeds ripen. A decrease in the quantity of glucoside would appear plausible if one holds to the theory that its function is to sterilize any injury received by the fruit and thus prevent further injury from the introduction into the wound of molds and bacteria. With the maturity of the fruit the need for this protection would cease to exist.

Upon receipt, the seeds were immediately shelled, placed in the oven and dried, and then ground. In some cases the oil was removed by extraction in a large syphon-extraction apparatus, by means of petroleum ether; in others most of the oil was removed by expression as is done in the preparation of amygdalin from almonds; in some others the original ground seeds were extracted with alcohol, which extracted only a small amount of the oil, but removed the glucoside. By evaporation to dryness and extraction of this residue with ether the oil could all be removed and the black gummy residue treated for the isolation of gynocardin.

[6] Dox, A. W., *Plant World* (1912), 15, 40.

Where immature nuts were being handled, the most successful method for their treatment was the following: The ground nuts were triturated with hot water, allowed to stand for some time, expressed, and the process repeated. The water was removed by distillation in a partial vacuum, the black gummy mass was triturated repeatedly with hot 90 per cent alcohol, and the alcohol was removed by distillation in a partial vacuum or more slowly at not too high a temperature at atmospheric pressure. The residue was repeatedly extracted, this time with hot absolute alcohol, and ether was added to the extract until a precipitate no longer formed. The extract was evaporated to dryness, and the residue was washed a number of times with acetone in the cold. In some instances this treatment left a semiviscous mass that could be crystallized from water. In a few instances the residue was dissolved in hot acetone and the acetone evaporated. However, gynocardin is not readily soluble in acetone, and as a small amount of fat persistently adheres to the glucoside and this is dissolved by the acetone along with the glucoside, dissolving in water preceded by washing with cold acetone was found to be more successful in obtaining a pure crystalline compound. Crystallization will not take place in the presence of a small amount of the oil; consequently its removal was necessary. The compound was obtained in the form of hairlike, golden yellow crystals, with a melting point of 160° C. The yield of the pure substance was between 0.2 and 0.3 per cent based on the weight of the dry kernels of the immature nuts. In another sample of immature seeds a quantitative estimation of the hydrocyanic acid was made by suspending 4 grams of the ground seeds in water and hydrolyzing them at a temperature of 39° C. with emulsin. At the end of forty-eight hours the hydrocyanic acid was distilled into sodium hydroxide containing a trace of potassium iodide and the latter was titrated to opalescence with 0.01 *N* solution of silver nitrate. This procedure indicated a content of 0.0126 per cent of hydrocyanic acid corresponding to 0.156 per cent of gynocardin.

## PROPERTIES OF GYNOCARDIN

The best known hydrocyanic glucoside is amygdalin.[6] Within recent years many new ones have been discovered, and their properties have been studied. The chemical properties of the cyanogenetic glucoside, gynocardin, have been noted by De Jong

[6] Abderhalden, Emil, Biochemisches Handlexikon. Julius Springer, Berlin (1911), 2, 707.

and by Power and Lees in the references cited. For purposes of identification, the melting point and specific rotation of the compound isolated by me were determined, and comparison was made with those of the products isolated by these works.

TABLE I.—*Melting point and specific rotation of gynocardin.*

| | Source. | | |
|---|---|---|---|
| | Seeds of *Gynocardia odorata.*[a] | Leaves of *Pangium edule.*[b] | Seeds of *Pangium edule.*[c] |
| Melting point..°C... | 162–163 | 160–161 | 160–161 |
| Specific rotation in chloroform solution. | $[\alpha]^{21^\circ}_{D}=+72.5^\circ$ | $[\alpha]^{28^\circ}_{D}(1.77\ \%)=+69.7^\circ$<br>$[\alpha]^{28^\circ}_{D}(16.885\%)=+62.2^\circ$ | $[\alpha]^{30^\circ}_{D}(2.5\%)=+63.2^\circ$ |

[a] Powers and Lees, loc. cit. [b] De Jong, loc. cit. [c] Occurring in the Philippine Islands.

The properties of the compound isolated from the seeds of *Pangium edule* are so nearly identical with those of the glucoside from the seeds of *Gynocardia odorata* and from the leaves of *Pangium edule* that no doubt exists as to their identity. De Jong found that the concentration of the chloroform solution had considerable influence on the specific rotation of the compound. This fact is apparent in the results quoted above from his publication.

Gynocardin differs from the other members of this class of compounds in its marked stability in the presence of acid hydrolyzing agents. It also hydrolyzed very slowly by emulsin.

TABLE II.—*Hydrolysis of gynocardin by means of emulsin.*

| Time. | Quantity of gynocardin. Solution of 2 grams in 300 cc. water. | Quantity of emulsin. | Quantity of other substance added. | Glucoside hydrolyzed. |
|---|---|---|---|---|
| *Min.* | *cc.* | *Grams.* | | *Per cent.* |
| 20 | 25 | 0.05 | none | 0.68 |
| 40 | 25 | 0.05 | none | 0.72 |
| 60 | 25 | 0.05 | none | 0.76 |
| 20 | 25 | 0.10 | none | 0.96 |
| 40 | 25 | 0.10 | none | 1.02 |
| 60 | 25 | 0.10 | none | 1.08 |
| 20 | 25 | 0.05 | [a]0.20 | 0.52 |
| 40 | 25 | 0.05 | [a]0.40 | 0.40 |
| 60 | 25 | 0.05 | [a]0.80 | 0.48 |
| 20 | 25 | 0.05 | [b]1 | 2.05 |
| 40 | 25 | 0.05 | [b]5 | 1.94 |
| 60 | 25 | 0.05 | [b]10 | 0.52 |

[a] Glucose in grams.
[b] Hydrocyanic acid in cubic centimeters of 0.1 per cent solution.

Auld[7] has determined the rate of hydrolysis for amygdalin by means of emulsin. Amygdalin reacts much more rapidly with emulsin as well as with acids than does gynocardin. His results with emulsin in the presence of added glucose and of added hydrocyanic acid are in accord with the results obtained by me for gynocardin, namely, the glucose inhibits the reaction, the amount being dependent on the relative quantity of glucose added, while hydrocyanic in smaller amounts accelerates the action, but when added in larger quantities the inhibiting effect is apparent. He has also found that the law of mass action does not hold good in its entirety for enzymic action. A large excess of the substrase does not cause a like increase in the rate of reaction when this addition has proceeded beyond a certain limit. The enzyme appears to be capable of reacting with only a certain amount of the substrase in a stated interval of time, and as long as the amount of this substrase exceeds a certain limit, no acceleration of the reaction takes place on the addition of more of the substrase. On the other hand, an increase in the amount of the enzyme gives a corresponding acceleration of the reaction, if the substrase is present in excess to react with the original amount of enzyme present. In the preceding table addition of more emulsin has accelerated the reaction.

The juice from the crab contains a secretion which hydrolyzes amygdalin giving hydrocyanic acid. To examine gynocardin in this respect, a series of experiments was undertaken. The juice of crabs, purchased in the local market, was obtained by expression, and comparative tests were made with it on amygdalin and gynocardin.

TABLE III.—*Action of crab juice on 1 per cent solutions of gynocardin and of amygdalin.*

| Time. | Glucoside. | Glucoside. | Crab juice. | Glucoside hydrolyzed. |
|---|---|---|---|---|
| *Hours.* | | *cc.* | *cc.* | *Per cent.* |
| 24 | Amygdalin | 25 | 10 | 51.99 |
| 24 | Gynocardin | 25 | 10 | 11.60 |
| 28 | Amygdalin | 25 | 10 | 69.10 |
| 48 | Gynocardin | 25 | 10 | 13.16 |
| 71 | Amygdalin | 25 | 10 | 75.67 |
| 71 | Gynocardin | 25 | 10 | 17.18 |

According to Table III gynocardin is likewise attacked more slowly by crab juice than is amygdalin. Toluene was added in

[7] Auld., S. J. Manson, *Journ. Chem. Soc. London* (1908), **93**, 1251.

the above case for an antiseptic. The flasks containing the solutions were incubated at 39° C.

In view of the hydrolyzing effect of crab juice it was thought that it might prove interesting to determine the effect of adding blood to similar samples.

TABLE IV.—*Action of blood on a 1 per cent solution of gynocardin.*

| Time. | Kind of blood. | Blood. | Glucoside. | Glucoside hydrolyzed. |
|---|---|---|---|---|
| *Hours.* | | *cc.* | *cc.* | *Per cent.* |
| 21.5 | Blood from apparently healthy person | 3 | 25 | 1.45 |
| 21.5 | Blood from tubercular patient (rather advanced case) [a] | 3 | 25 | 1.69 |
| 22.5 | Blood from syphilitic person | 6 | 25 | 3.63 |
| 45.5 | Blood from apparently healthy person | 3 | 25 | 3.15 |
| 45.5 | Blood from tubercular patient (fairly advanced case) [a] | 3 | 25 | 6.14 |
| 46.0 | Blood from syphilitic person | 6 | 25 | 3.96 |

[a] This blood was kindly furnished me by Dr. J. W. Smith, in charge of Bilibid Prison.

The above results indicate that blood from tubercular patients reacts more rapidly with gynocardin than does the blood of the normal person. The blood from the syphilitic person apparently reacted more rapidly the first day, but the sample incubated two days reacted no faster than the sample from the normal person. The Bureau of Science has collected some further data concerning this property when amygdalin is used that substantiates the above evidence.

Amygdalin has been found to be harmless when taken into the system unless administered in the presence of emulsin. Gynocardin, when given in doses of 0.25 and 1 gram to guinea pigs, was found to be without any apparent effect. At the end of twenty-four hours no further observations were taken, as the pigs appeared perfectly normal.

## GYNOCARDASE

The enzyme gynocardase was obtained from the leaves of *Pangium edule* by grinding the leaves very fine and then pressing in a hydraulic press, adding an equal volume of alcohol to the juice and filtering. The precipitate was then ground under water with sand, filtered through cloth, and again precipitated by the addition of alcohol. The precipitate was nearly black

and of gummy consistence. Determinations of its activity were made with amygdalin and gynocardin.

TABLE V.—*Activity of gynocardase on 1 per cent solutions of amygdalin and gynocardin.*

| Time. | Glucoside. | | Enzyme. | Glucoside hydrolyzed. |
|---|---|---|---|---|
| *Hours.* | | *cc.* | *Grams.* | *Per cent.* |
| 24 | Amygdalin | 25 | 0.2 | 25.57 |
| 24 | do | 25 | 0.2 | 26.02 |
| 24 | Gynocardin | 25 | 0.2 | 13.82 |
| 24 | do | 25 | 0.2 | 13.28 |

Here again gynocardin is less readily hydrolyzed than amygdalin. Since gynocardin is hydrolyzed by emulsin, which is a $\beta$-enzyme, it must be a $\beta$-glucoside.[8]

Gynocardase hydrolyzes both gynocardin and amygdalin; consequently it must belong to the class of $\beta$-enzymes typified by emulsin.

Several samples of nuts were examined for their oil content.

TABLE VI.—*Oil content and properties of oil obtained from the seeds of Pangium edule.*

| | Mature. | Immature. |
|---|---|---|
| | *Per cent.* | *Per cent.* |
| Kernel content of air-dried nuts | 42.67 | 36.38 |
| Dried kernel content based on air-dried nuts | 29.09 | 16.28 |
| Oil content based on dried kernels | 21.09 | 24.11 |

| | Free acids from oil of mature seeds. | Oil from mature seeds. | Free acids from oil of immature seeds. | Oil from immature seeds. |
|---|---|---|---|---|
| Melting point | Clouds at 18° C. | Shows some clouding at 2° C. | | No change at 8° C. |
| Specific gravity | 0.9013 | 0.9049 | 0.8955 | 0.9092 |
| Specific rotation in chloroform solution | +3.49 | +4.28 | +4.72 | +20.65 |
| Iodine value (Hanus) | 113.5 | 113.1 | 103.0 | 109.5 |
| Acid value cc. 0.1 *N* alkali | 36.7 | 0.52 | 34.2 | 0.90 |
| Saponification value | 207.8 | 190.3 | 205.4 | 188.3 |
| Index of refraction | 1.4582 | 1.4665 | 1.4595 | 1.4675 |

[8] Fischer, E., *Ber. d. deutsch. chem. Ges.* (1894), 27, 2985.

To determine the physiological activity of the oil, 2 grams and 2.5 grams, respectively, were administered per os to each of two guinea pigs. No ill effect was noted in either case.

Owing to the limited quantities of the nuts available, no exhaustive study of the oil could be made. However, enough was obtained to determine that palmitic and oleic acids and small quantities of an optically active acid are present. The latter may be either hydnocarpic or chaulmoogric or a mixture of the two. It resembles chaulmoogra and the hydnocarpus oils by the presence of an optically active oil.

### HYDNOCARPUS ALCALÆ C. DE CANDOLLE

A sample of the fruit of *Hydnocarpus alcalæ* C. de Candolle [9] was submitted by the Bureau of Agriculture to the Bureau of Science for identification and examination. It had been sent to the Bureau of Agriculture by Mr. T. Alcala, of Daraga, Albay Province, Luzon, under the local name *dudu dudu*. It was large, somewhat resembling a small unhusked coconut, about 20 centimeters long and 15 centimeters in lateral dimensions. Within the pericarp were numerous seeds, measuring 4 centimeters by 2.5 centimeters.

Mr. Alcala writes:

> It is said that the oil extracted from the seeds is a good cure for wounds. It is generally believed to be poisonous, and when I ate six or eight of the boiled seeds I had a slight sickness; however, many children eat them raw without the slightest ill effect.

At the suggestion of Mr. E. D. Merrill, botanist, Bureau of Science, that this fruit belongs to the *Hydnocarpus* family, an examination was made for hydrocyanic acid. The presence of this acid would indicate the existence of a cyanogenetic glucoside. All such tests resulted negatively. However, the fresh fruit or the unripe fruit might contain such bodies. Our examination of *Pangium edule* has shown that a decrease or complete disappearance of the glucoside results when the nuts age, unless the hydrolyzing enzyme is destroyed, and that with the ripening of the nut a decrease in the glucoside content probably occurs. Consequently the inability to obtain positive tests in this one sample of seeds for hydrocyanic acid is not to be considered as sufficient proof to warrant the statement that no cyanogenetic glucoside exists at any period in the growth of the fruit.

[9] De Candolle, C., *This Journal, Sec. C* (1916), **11**, 37.

TABLE VII.—*Properties of nuts and oil of Hydnocarpus alcalæ.*

| | | |
|---|---|---|
| Average weight of fruit | grams | 420 |
| Hulls | per cent | 59.68 |
| Seeds | do | 40.32 |
| Moisture in seeds | do | 60.50 |
| Oil in dry seeds | do | 65.50 |
| Melting point | degrees | 32 |
| Specific gravity at 30° C. | | 0.9502 |
| Specific rotation in chloroform | degrees | +49.60 |
| Iodine value (Hanus) | | 93.10 |
| Acid value cc. 0.1 *N* alkali | | 3.90 |
| Saponification value | | 188.90 |
| Index of refraction | | 1.4770 |
| Reichert Meissl No. | | 4.43 |

The nuts and the extracted oil were administered per os to chickens without any noticeable ill effects.

The free acids of the oil from *Hydnocarpus alcalæ* were examined.

TABLE VIII.—*Properties of the free acids of the oil from Hydnocarpus alcalæ.*

| | | |
|---|---|---|
| Melting point | degrees | 59 |
| Specific gravity at 30° C. | | 0.9342 |
| Specific rotation in chloroform 30/D | degrees | 53.65 |
| Iodine value (Hanus) | | 98.6 |
| Acid value cc. 0.1 *N* alkali | | 37.4 |
| Saponification value | | 193.0 |

The free acids were then treated as described by Power for the separation of chaulmoogric acid. More than 90 per cent of these acids consist of a compound identical in properties with the acid designated as chaulmoogric by Power.

TABLE IX.—*Properties of the acid isolated from the oil from Hydnocarpus alcalæ.*

| | | |
|---|---|---|
| Melting point | degrees | 68–69 |
| Specific rotation in chloroform 30/D | do | +59.69 |
| Iodine value (Hanus) | | 89.7 |

0.3400 gram of silver salt gave 0.0950 gram of silver, equal to 27.94 per cent silver.

0.5040 gram of sodium salt gave 0.1206 gram of sodium sulphate equal to 7.75 per cent sodium.

Theoretical for $C_{17}H_3$ COO Ag=27.86 per cent silver.

Theoretical for $C_{17}H_3$ COO Na=7.62 per cent sodium.

Only a small amount of the acids remained in the mother liquor. No hydnocarpic acid could be isolated from this. The latter exists in very small quantities in *Hydnocarpus alcalæ* if at all. Palmitic acid makes up the chief part of the remaining

portion with only traces of oleic acid. Both of these oils differ greatly in melting points from the oils from chaulmoogra and *Hydnocarpus* reported by Power and his coworkers.

*Pangium edule* contains a large amount of olein and smaller quantities of palmitin.

If hydnocarpic and chaulmoogric esters are specific for leprosy, *Pangium edule* oil would be an admirable remedy to use, since it would be easy to administer because of its low melting point and consequent fluidity, but would probably be slow in its action on account of the relatively small amounts of these acids present. On the other hand, *Hydnocarpus alcalæ* oil would be much more difficult of administration because of its being a solid even at the ordinary temperature in Manila (30°C.).

## SUMMARY

The report of an investigation of the oils from *Pangium edule* and *Hydnocarpus alcalæ* and of the cyanogenetic glucoside, gynocardin, is given. Their properties are discussed in some detail.

# REVIEW

**A Laboratory Guide | to the Study of | Qualitative Analysis | based upon the |** Application of the Theory of | Electrolytic Dissociation | and the Law of Mass Action | by | E. H. S. Bailey, Ph. D. | professor of chemistry in the University of Kansas | and | Hamilton P. Cady, Ph. D. | professor of chemistry in the University of Kansas | Eighth Edition | revised by | Paul V. Faragher, Ph. D. | assistant professor of chemistry in the University of Kansas | in collaboration with the authors | Philadelphia | P. Blakiston's Son & Co. | 1012 Walnut street | Copyright, 1916. Cloth pp. i–x+1–294. Price $1.50.

The eighth edition of Professors Bailey and Cady's book, revised by Assistant Professor Faragher, is essentially the same as the seventh edition except for some minor modifications, consisting in the amplification of some sections difficult of comprehension by the student.

The scope and volume of this edition is, in general, the same as that of previous editions. The introductory part covers 24 pages; 126 pages are devoted to the reactions of the cations and a table for their systematic analysis, and 117 are taken up with the anions, also with a table for their systematic analysis. None of the rare metals are treated, except gold and platinum. A table for use in the examination of an unknown substance and another table of solubilities close the text.

The introductory portion is furnished with a brief and accurate discussion of electrolytic dissociation and the mass action law as it is applied to qualitative analysis. The experiments given for the reactions of the individual ions are well selected; the tables for the separation of cations and anions into groups and the tests for their identification includes some good tests, for example, the dimethyl glyoxime reaction with nickel ions; while such subjects as hydrolysis, oxidation, and reduction are treated clearly in proper places in the book, thus rendering it easy for the student to comprehend their practical application.

The mechanical details of the book are good and misprints are few (p. 68, $4H_4O$ instead of $4H_2O$). The type is clear, and the illustrated tables are well gotten up.

On the whole, the book is a good, brief laboratory guide for students in qualitative analysis.

F. PEÑA.

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## Section A

## CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

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THE PHILIPPINE

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## THE STUDY OF COPRA AND OTHER COCONUT PRODUCTS[1]

By ALVIN J. COX

*(From the Bureau of Science, Manila)*

For several years the chemists, assisted by the botanists, of the Bureau of Science have been employed, as time permitted, in a study of the products of the coconut. Many investigations have been made and published by the Bureau of Science on the subject.[2] Coconut oil as such and in the unpressed copra ranks among the three most important exports from the Philippine Islands and, therefore, warrants careful study. There are two large operating vegetable oil plants in the Philippine Islands,

[1] Received for publication February, 1917.

[2] Freer, Paul C., On the water relations of the coconut palm (Cocos nucifera)—On the oil produced from the nuts—The factors entering into the rancidity of the oil—The insects attacking the trees—Introduction, *This Journal* (1906), **1**, 3–5. Copeland, E. B., On the water relations of the coconut palm (Cocos nucifera), ibid. (1906), **1**, 6–57. Walker, Herbert S., The coconut and its relation to the production of coconut oil, ibid. (1906), **1**, 58–82. Walker, Herbert S., The keeping qualities of coconut oil and the causes of its rancidity, ibid. (1906), **1**, 117–142. Banks, Charles S., The principal insects attacking the coconut palm, ibid. (1906), **1**, 143–168, 211–228. Richmond, George F., Purification of coconut oil, ibid., *Sec. A* (1908), **3**, 45–47. Walker, Herbert S., Notes on the sprouting coconut, on copra, and on coconut oil, ibid., *Sec. A* (1908), **3**, 111–135. Gibbs, H. D., and Agcaoili, F., On the detection and determination of coconut oil, ibid., *Sec. A* (1908), **3**, 371–375. Pratt, David S., Copra spoilage on a large scale, ibid., *Sec. A* (1913), **8**, 439–441. Pratt, David S., The coconut and its products with special reference to Ceylon, ibid., *Sec. A* (1914), **9**, 177–199. Brill, Harvey C., Parker, Harrison O., and Yates, Harry S., Copra and coconut oil, ibid., *Sec. A* (1917), **12**, this number. Parker, Harrison O., and Brill, Harvey C., Methods for the production of pure coconut oil, ibid., *Sec. A* (1917), **12**, this number.

and several small ones are now being erected or planned. The work of the Bureau of Science has been done from time to time in order to settle some special problem, and all of it has been beneficial in pointing the way to more extended problems. The studies by Walker [3] on the keeping qualities of coconut oil and the causes of its rancidity and notes on the sprouting coconut, on copra, and on coconut oil have been very helpful to the public, and his papers have been in great demand. For several years we have endeavored to find time to continue and extend this work and to accumulate information with regard to the composition of the coconut, the hydrolysis and consequent destruction of fat, the methods of drying, the methods for the most effective recovery of the oil, the methods of analysis, the detection of adulterants of coconut oil and of coconut oil as an adulterant of other oils, and the reduction to a minimum of the loss through deterioration of copra and coconut oil during transportation. Data showing the composition of many Philippine soils have been published, and some of these concern the soils from the best coconut areas.

In recent years I have been impressed by the large loss of coconut oil through spoilage and the unearned revenue that the Philippine Islands would secure if all the copra produced were of a high grade. Furthermore there is a loss in shipping poorly cured copra, not only in the deterioration due to mold and bacterial action, but also in the transportation of the excess moisture.

The work begun by Dr. Paul C. Freer and by Mr. H. S. Walker has been continued by Dr. Harvey C. Brill and Mr. Harrison O. Parker, the botanical work being done by Dr. Harry S. Yates.

In California large quantities of deciduous fruits are opened, treated with sulphur dioxide (the fumes of burning sulphur) to protect them from bacterial or mold action, and subsequently dried. The action of sulphur dioxide is to kill all mold spores and to soften the cell walls of the fruit so that drying is facilitated. Enough of the sulphur dioxide remains in the meat to prevent the growth of new mold spores during drying, if drying is completed in a week or two.

We have successfully applied this method to the drying of coconut meat. Coconuts opened and treated with the fumes of burning sulphur at the Bureau of Science during a severe rainstorm, which subsequently received no artificial drying or exposure to the sunshine, remained perfectly white for a period

[3] Loc. cit.

of two weeks. Copra on hand after many months is still of excellent quality. The box in which the treatment with sulphur dioxide is made must be fairly tight, but not air-tight. There must be circulation enough to keep the sulphur burning. In the *tapahan* (Filipino grill for drying coconut meat) method of drying copra the coconut meat frequently begins to mold before the drying is begun, and before the drying has proceeded far enough to inhibit the growth of mold, considerable deterioration has taken place. In the sulphur process the nuts can be subjected to sulphur dioxide before mold has started to grow. With proper organization and routing of the work, the labor cost when the sulphur dioxide method is used will not exceed that in the tapahan.

Compared with the tapahan method the sulphur dioxide process is exceptionally clean: the copra is preserved and bleached by the sulphur dioxide and yields very white copra; there is no loss of oil during the treatment or during the drying; an exceedingly uniform copra is obtained, and its keeping quality is improved; and the oil expressed from the copra is practically colorless, is free from rancidity, is pronounced equal to, or better than, the best Cochin oil, and usually will sell for at least 10 centavos[4] a kilogram (2 cents or more a pound) more than ordinary oil. At 10 centavos a kilogram there is a difference of about 4 pesos per 63.25 kilograms (1 picul) of copra. Storage conditions and the problem of storage must receive careful consideration even with first-class copra; however, this will become less and less of a problem as more and more of the Philippine copra is consumed in local oil mills.

Other experiments have been in progress in an effort entirely to eliminate the drying process and to extract the oil from fresh coconut meat.

Lack of means for producing a good grade of copra or oil from the fresh nut has not been the only obstacle in the way of the improvement of the coconut industry. Most dealers have been contented with a poor copra and could not see any advantage to themselves in being able to secure a better product with a higher oil content. Dealers say that it has been their custom to put good copra with the poor, but the vegetable-oil companies will buy the good copra at a premium as soon as they can get enough to run a mill for a day or two once or twice a month. Many dealers now realize that properly dried copra is worth

[4] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

more—not only in proportion to the reduced water content, but also on account of its improved keeping qualities and the higher grade and value of the oil that can be obtained from it. If necessary, it will be productive of great results for the Government to penalize smoked, colored, dirty, moldy, or imperfectly dried copra and to subsidize the higher grades of copra until dealers become aroused and demand them, which they certainly will do in time. Such action will not only protect the consumer, but will increase the revenue of the producer. In order to establish definite grades and a certain market, a satisfactory system of classification and standards must be devised, as the Bureau of Science has long been advocating. At present no definite grades for a given region exist, owing to the unwillingness of the inhabitants properly to dry the copra. In the Manila markets the terms Cebu sundried, fair marketable Manila, and Laguna are known, although ill defined. Cebu sundried usually commands about 75 centavos per 63.25 kilograms (1 picul) more than Laguna. A step toward the solution of the question of standardization has been made by the Visayan Refining Company. Nine months of experience gave this company 65.5 per cent oil in the Cebu sundried copra used in its mill. The company has taken this as the average for a good grade of copra in the Cebu market, and for such copra it pays the market price and, in addition, when the copra is white, guarantees the consignee premiums for additional oil content as follows:

| Oil in white copra. Per cent. | Premium per 63.25 kilograms (1 picul). Centavos. |
|---|---|
| 66 | 12.5 |
| 67 | 25. |
| 68 | 37.5 |

By this system the producer cannot lose, and the possibility of receiving a bonus is an incentive to dry properly and to produce a higher grade copra.

In order satisfactorily to establish grades of copra, certain facts must be considered. Well-prepared copra is white, but the discoloration of black copra may be due to its being smoked when dried on the tapahan or to mold action. Copra is either wet or dry. There are various degrees of wetness. The following paper indicates the permissible amount of water if copra is expected to be mold-free in storage. The character of copra depends to a certain extent upon the variety of the nut and the region in which it is grown; therefore it is probable that it will be necessary to establish regional grades of copra. It is my opinion that on the basis of oil content in relation to moisture

content, cleanliness and freedom from dust, foreign matter or adulteration, free fatty acids, freedom from unripe nuts, and color and general appearance uniform rational grades for copra can be established throughout the Philippine Islands. The use of green nuts for copra in Samoa is prohibited. There is a law which provides that nuts for making copra must be allowed to drop from the trees. There are varieties of Philippine coconuts whose nuts do not drop when ripe. Oil content alone does not define a good copra, as the oil content of badly molded copra may be on a par with that of properly prepared copra, owing to the simultaneous destruction by molds of oil and of tissue in relative proportions. Also the oil content of the coconuts may vary with the region in which they are grown or with the variety of the nut. The enforcement of grading should be easy, for the color and appearance can be readily determined by inspection, and an inspector should soon become sufficiently expert tc judge the quantity of moisture by feel. There are also several simple tests that may be applied to substantiate his judgment. If copra is excessively wet, it is usually hot; if sufficiently dried, a piece of copra breaks when the two edges are pressed together. The width of the dark line showing on the fresh broken edge is a criterion of the moisture content. An expert can also judge of the oil and water content by lighting a sliver of copra. If it burns readily, the copra is fairly dry and has a high oil content; if it is moderately wet, the flame will sputter as the moisture is evaporated; if very wet, it will not burn.

The studies that follow contribute to our knowledge of copra and coconut oil and outline the means of obtaining a less acid and less rancid oil; this will command a higher market price and will bring the Philippines to the front for the quality of its copra and its coconut oil; this, in turn, will increase the revenue from Philippine coconut plantations.

# COPRA AND COCONUT OIL [1]

By Harvey C. Brill, Harrison O. Parker, and Harry S. Yates

*(From the Laboratory of Organic Chemistry, Bureau of Science, Manila)*

Increasing demands for fatty foodstuffs have developed the vegetable-butter industry in the United States—an industry formerly restricted to England, Holland, and France. Refineries and hydrogenation plants have been able to purify and harden practically all of the animal and vegetable oils suitable for edible purposes into either simple or compounded vegetable lards and butters. The oil obtained from the coconut ranks high in importance among these. However, an enormous amount of coconut oil is at present being used in the soap and glycerin industries, rather than for the manufacture of edible products, because of the poor quality of the commercial oil and its consequent cheapness.

The production of copra constitutes one of the leading industries of many tropical countries. In the Philippine Islands practically the entire annual crop of about 431,387,000 nuts,[2] with the exception of those used for local consumption, is turned into copra. Copra exports from the Philippine Islands for 1916 were 72,277,164 kilograms, and oil exports were 16,091,169 kilograms.[3]

The annual exports represent approximately one third of the world's output of copra,[4] most of which finds its way to the mar-

[1] Received for publication February, 1917. The isolation and study of the molds growing on Philippine copra were made by Harry S. Yates, of the section of botany, Bureau of Science.

[2] Cox, Alvin J., *Bureau of Science Press Bull.* (1916), No. 54. Computed from the yield of copra and based on the experiments of the Bureau of Science, which show that for the Philippine Islands 1,000 nuts yield about 270 kilograms of copra.

[3] Information furnished by the Insular Collector of Customs April 17, 1917.

[4] Smith, H. H., Coconuts. The Consols of the East. 2d ed. Tropical Life, London (1913), 362. Lewkowitsch, Chemical Technology and Analysis of Oils, Fats and Waxes. Macmillan & Co. Limited, London (1914), 22, 635.

kets of Great Britain, France, Holland, and the United States. There are but three modern coconut oil mills in operation in the Philippine Islands. These, together with the native mills, exported oil to the value of 5,641,003 pesos [5] in 1915.[6]

It is surprising to note that Philippine copra is quoted the lowest on the world's market. By calculating the value of Ceylon copra exported from 1908 to 1911 and comparing the figures with the value received for Philippine copra during the same period, it is found that the annual difference between what the Philippine Islands received and what they should have received in 1911 [7] is more than 4,000,00 pesos and for the previous five years is more than 15,000,000 pesos.

The reason for the low price is found in the poor quality of copra produced. Some attention has been paid of late years to the improvement of the quality, but concerning the cause of this inferiority only a little published data is available. Oil obtained from the usual Philippine copra is discolored and rancid and contains free fatty acids varying from 5 to 20 per cent (oleic acid). These conditions favor even further deterioration of the oil.[8] The quality of the oil depends primarily upon the condition of the copra at the time it is milled, and poorly prepared copra deteriorates rapidly with loss of oil and impairment of its quality. The poor quality of the copra is due to insufficient drying and unclean methods used in its production. It is the purpose of this paper to bring out analytical and botanical data relative to losses in copra and oil due to the faulty production of copra and to suggest means for improvement. Unless coconut meat is dried, immediately after opening the nuts, to a moisture content of approximately 6 per cent, it is attacked by various microörganisms, which causes a loss in oil content. The extent of the loss depends upon the length of time the meat retains sufficient moisture for mold growth.

It was determined by experiment and observation that molds grow most luxuriantly upon copra with a moisture content of 10 per cent or greater, which, as shown in Table I, is common in commercial copra.

[5] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

[6] *Annual Rep. P. I. Bur. Customs* (1915), 17, 18.

[7] Pratt, D. S., *This Journal, Sec. A* (1914), **9**, 186.

[8] Walker, H. S., *This Journal* (1906), **1**, 141.

TABLE I.—*Moisture content of copra samples from various localities in the Philippine Islands.*

| Locality. | Water. | |
|---|---|---|
| | Maximum. | Minimum. |
| | *Per cent.* | *Per cent.* |
| San Pablo, Laguna | 29.1 | 18.8 |
| Lucena, Tayabas | 23.1 | 14.6 |
| Legaspi, Albay | 22.2 | 17.6 |
| Tacloban, Leyte | 20.7 | 14.4 |
| Atimonan, Tayabas | 24.7 | 15.5 |
| Borongan, Samar | 14.1 | 10.4 |

It was deemed essential to determine the loss in weight of commercial copra stored and handled under ordinary conditions, especially as laboratory experiments conducted on copra under the most favorable moisture conditions for mold growth (10 to 20 per cent) showed a loss of 25 per cent in total oil content. Table III gives losses for copra stored in bodegas. The data in Table II were obtained by analysis of partially dried copra stored in a container at room temperature for fifteen days. The moisture conditions were regulated throughout the experiment to favor maximum mold growth, that is, from 10–20 per cent water. The loss represents the combined action of green, brown, black, and white molds.

TABLE II.—*Effect of the four common molds—green, brown, black, and white—growing together on copra.*

| Series No. | Weight of copra. | Oil in copra before mold action. | Oil after mold action. | Loss of oil. | | Acidity as oleic acid after mold action.[a] |
|---|---|---|---|---|---|---|
| | *g.* | *g.* | *g.* | *g.* | *Per cent.* | *Per cent.* |
| 1 | 17.10 | 5.0838 | 3.8138 | 1.2700 | 24.9 | 15.6 |
| 2 | 17.50 | 5.2027 | 3.8882 | 1.3145 | 25.2 | 12.4 |
| 3 | 16.62 | 4.9411 | 3.7369 | 1.2042 | 24.3 | 13.0 |
| 4 | 15.96 | 4.3571 | 3.3167 | 1.0404 | 23.8 | 9.0 |
| 5 | 16.14 | 4.7984 | 3.4468 | 1.3516 | 28.1 | 11.4 |
| 6 | 84.20 | 25.0326 | 18.6020 | 6.4306 | 25.6 | 10.0 |

[a] Acidity of oil expressed from fresh coconut meat is always about 0.2 per cent calculated as oleic acid.

It is obvious that if there is a loss in oil there must also be a loss in weight of the copra from this source. Buyers of copra recognize that a loss in weight occurs when copra is stored, and they are governed in their purchase by this factor. The loss in weight when commercial copra is stored is shown in Table III.

TABLE III.—*Loss in weight of copra from various provinces when stored in commercial bodegas.*

| Place of production. | Days stored. | Loss in weight. |
|---|---|---|
| Albay Province: | | *Per cent.* |
| Legaspi | 29 | 9.61 |
| Do | 10 | 6.00 |
| Do | 22 | 1.00 |
| Camarines Province: | | |
| Daet | 28 | 0.00 |
| Do | 31 | 6.25 |
| Do | 12 | 2.5 |
| Do | 26 | 5.0 |
| Capiz Province: | | |
| Calivo | 29 | 8.77 |
| Do | 26 | 10.07 |
| Do | 20 | 4.5 |
| Jolo | 20 | 1.5 |
| Laguna Province: | | |
| Pagsanjan | 19 | 16.60 |
| Do | 28 | 8.41 |
| Do | 14 | 2.0 |
| Do | 25 | 10.25 |
| Do | 25 | 5.5 |
| Do | 20 | 12.25 |
| Do | 9 | 7.00 |
| San Pablo | 28 | 10.48 |
| Do | 26 | 12.71 |
| Do | 11 | 9.25 |
| Pangasinan Province: | | |
| Dagupan | 19 | 8.77 |
| San Carlos | 10 | 10.00 |
| Romblon | 29 | 3.87 |
| Do | 29 | 7.5 |
| Do | 25 | 11.5 |
| Magallanes | 28 | 2.86 |
| Do | 24 | 4.22 |
| Samar Province: | | |
| Catarman | 28 | 0.86 |
| Catbalogan | 20 | 2.5 |
| Sorsogon Province: | | |
| Bulan | 14 | 1. |
| Do | 21 | 1.5 |
| Gubat | 28 | 0.91 |
| Do | 24 | 10.22 |
| Do | 18 | 6.38 |
| Do | 18 | 8.15 |
| Surigao Province | 23 | 5.5 |

TABLE III.—*Loss in weight of copra, etc.*—Continued.

| Place of production. | Days stored. | Loss in weight. |
|---|---|---|
| Tayabas Province: | | *Per cent.* |
| Atimonan | 25 | 1.00 |
| Do | 30 | 0.4 |
| Boac | 28 | 17.74 |
| Do | 26 | 12.97 |
| Do | 19 | 1.75 |
| Candelaria | 20 | 12.07 |
| Do | 29 | 14.58 |
| Guinayañgan | 28 | 2.90 |
| Infanta | 18 | 1.75 |
| Lucena | 18 | 6.53 |
| Do | 31 | 18.69 |
| Do | 18 | 9.09 |
| Do | 12 | 14.05 |
| Do | 14 | 9.75 |
| Do | 24 | 8.00 |
| Do | 23 | 10.00 |
| Pagbilao | 29 | 7.50 |
| Do | 15 | 8.06 |
| Sariaya | 25 | 12.5 |

There is a further loss in weight of copra on shipboard, which the copra dealers estimate at from 3 to 6 per cent, depending primarily upon the length of time of storage before shipment. With the high freight rates that have prevailed for the past year for copra shipments to the United States, the loss due to paying freight on loss of weight alone is considerable; even under normal conditions this loss is too large to be ignored.

Freight rates at 50 pesos per ton with loss in weight of 6 per cent amount to 3 pesos for each ton of copra. When the product is not completely dried, there results not only an unnecessary expense of handling an excessive amount of water, but also the conditions are most favorable to mold growth with consequent loss in quality and quantity of the oil. It is the producer who suffers,[9] for the purchaser reduces the price to cover not only the extra water, but also the extra handling and transporta-

[9] While the price paid to the producer is less for his poor product than it would be for a higher grade product, some question exists as to his suffering any excessive monetary loss. Consideration should be given to the fact that he has no great amount of money invested in apparatus, that he can employ unskilled labor, and that he expends no great amount of care in the preparation of his product. The difference in the cost of producing poor and of producing good copra is hardly made up by the present discriminating price. The production of poor copra should rather be considered an economic loss to the Philippine Islands.

tion expenses. That these losses incident to storage and shipment extending over periods of from two to four months are not due entirely to the evaporation of water is evident from Table IV, showing temperature, carbon dioxide, and weight loss relationship of stored Laguna copra. It is obvious from these figures, which show an increased temperature with a corresponding increase in carbon dioxide over the normal atmosphere condition, that slow combustion is taking place with the formation of carbon dioxide and water, necessarily at the expense of the meat and the oil.

The increase in temperature of the copra parallels the increase in carbon dioxide content of the atmosphere surrounding the copra, rises to a maximum at the same time, and decreases along with the decrease of the carbon dioxide concentration, proving that the heat is produced by the combustion of the copra.

TABLE IV.—*Temperature and carbon dioxide relationship of commercial, stored copra. Temperature of atmosphere, 29° C.*

| Copra. | Date. | Temperature. | Carbon dioxide ($CO_2$) in atmosphere over stored copra. |
|---|---|---|---|
| | | *°C.* | *Per cent.* |
| Lot I | September 20 | 40 | 0.4 |
| | September 23 | 40 | 0.4 |
| | September 25 | 38 | 0.3 |
| | September 26 | 38 | 0.2–0.3 |
| Lot II | September 26 | 50 | 1.0 |
| | September 27 | 55 | 1.6 |
| | September 28 | 55 | 1.4 |
| | September 29 | 53 | 1.2 |
| | September 30 | 50 | 1.0 |
| | October 2 | 48 | 0.8 |
| | October 4 | 48 | 0.8 |
| | October 6 | 45 | 0.6 |
| | October 7 | 41 | 0.4 |
| | October 9 | 40 | 0.4 |
| | October 10 | 38 | 0.4 |
| | October 11 | 38 | 0.2 |
| | October 12 | 36 | 0.2 |
| | October 13 | 35 | 0.2 |
| Lot III | September 26 | 45 | 0.8 |
| | September 27 | 44 | 0.8 |
| | September 28 | 42 | 0.6 |
| | September 29 | 40 | 0.6 |
| | September 30 | 40 | 0.4 |
| | October 2 | 38 | 0.4 |
| | October 4 | 38 | 0.2 |
| | October 6 | 36 | 0.2 |

The data in Table IV was obtained by measuring the average temperature of a lot of copra with a moisture content corresponding to the commercial samples described in Table I. The quantity amounted to over 200 piculs. The carbon dioxide measurement was made by withdrawing air from the center of the pile and determining the percentage of carbon dioxide by means of a special absorption apparatus. The average temperature of the air outside was 29° C., and the percentage of carbon dioxide in the air was always less than 0.10.

Five bags belonging to lot II were weighed before and after storage in the general pile from which the carbon dioxide and temperature determinations were made.

TABLE V.—*Weight loss in commercial copra stored twenty-five days in bodegas.*

| Bag No. | Weight. | | |
|---|---|---|---|
| | September 26. | October 19. | Loss. |
| | *Kilos.* | *Kilos.* | *Per cent.* |
| 1 | 57 | 50 | 12.4 |
| 2 | 45 | 40.5 | 10.0 |
| 3 | 56 | 48.5 | 13.4 |
| 4 | 73.5 | 66.5 | 9.5 |
| 5 | 70.5 | 63 | 10.6 |

The copra in the general pile after storage was badly damaged, particularly the bags of the lower layers, which were matted together into a solid mass of black, foul-smelling, decayed material. It is not reasonable to presume that in a large pile of sacked copra much moisture will escape of its own accord. However, so long as moisture is sufficient in amount to cause mold growth, the combustion brought about within the pile, as was most evident during the periods of highest temperature conditions, causes liberation of the moisture. The cause for a decrease from a maximum temperature and from carbon dioxide conditions to normal is influenced by two factors—there is a loss in water to a point where the mold will not flourish, and the temperature reached by the copra is sufficient to inhibit if not entirely to destroy the mold spores.[10]

[10] Rather, J. B., *Journ. Ind. & Eng. Chem.* (1916), 8, 604, has shown that cottonseed containing a percentage of moisture greater than a certain maximum heats when piled and that this heating continues until the moisture content is lowered. An increase in the free fatty acids and a darkening of the oil are results of the heating.

Well-dried copra neither became hot nor evolved carbon dioxide when piled in storage, demonstrating that this combustion is due to the presence of higher quantities of moisture together with the consequent action of the mold.

Various factors enter into the analysis of copra from the point of view of oil loss. Curiously, only in exceptionally bad copra is the percentage of oil found materially lower than would be expected in good copra. This is due to the fact that both meat and oil are attacked by the microörganisms lowering the total weight of the sample. Therefore it is necessary that the total weight of the oil in the original piece of fresh meat be known in order that the percentage of total loss may be calculated from the actual weight of oil before and after deterioration.

Table VI shows the apparent loss of oil calculated from the percentages and the true loss in oil for the same piece of copra and clearly illustrates our statement above.

TABLE VI.—*Oil losses in copra calculated on oil percentages and on total oil content.*

| | Sample No.— | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Dry meat before mold action, calculated ........ grams | 13.5802 | 11.7834 | 13.2477 | 16.1955 | 13.3213 |
| Dry meat after mold action ........ do | 11.8390 | 10.2104 | 11.8089 | 14.4030 | 11.9880 |
| Oil in dry meat before mold action .. per cent | 67.5 | 67.5 | 66.8 | 66.8 | 66.8 |
| Oil in dry meat after mold action, calculated ........ per cent | 53.6 | 54.6 | 49.6 | 47.1 | 46.7 |
| Total oil before mold action, calculated ........ grams | 9.1645 | 7.9540 | 8.8386 | 10.8155 | 8.8744 |
| Total oil after mold action ........ do | 6.3465 | 5.5846 | 5.8570 | 6.7880 | 5.6010 |
| Apparent loss of oil from percentages ........ per cent | 13.9 | 12.9 | 17.2 | 19.7 | 20.1 |
| True loss of oil ........ do | 30.7 | 29.8 | 33.7 | 37.2 | 36.8 |

The above results conclusively show that the true loss of oil is very much greater than the apparent. The apparent change does not take into account the weight of the fiber destroyed; consequently the apparent loss is always smaller than the true loss and in certain instances might appear negligible or that there had been a synthesis of oil by mold growth. Indeed Walker,[11] in some experiments where he did not take this factor into consideration, obtained results which indicate a synthesis of oil by microörganisms. Such results show the worthlessness of data

[11] Op. cit., 117.

calculated on the basis of the molded sample for demonstrating the quantity of oil actually decomposed.

MICROÖRGANISMS AND THEIR EFFECT ON COPRA AND COCONUT OIL

Comparatively little attention has been given to the effect of microörganisms on coconut oil. Walker [12] has called attention to the fact that they do seriously affect the quantity and quality of the oil in copra. However, his experiments were few and devised primarily to show the action of the organisms on the oil irrespective of the amount of moisture present in the copra. When fresh coconut meat is exposed to the air, various fungi make their appearance, and as the moisture content of the meat becomes less, these fungi are succeeded by others. Certain fungi always appeared on the fresh meat and others on fairly dry copra, and so it seemed probable that each of the fungi concerned was restricted more or less closely to a definite condition of moisture in the copra. The life history of each of the more important organisms was studied to determine whether the effect on the oil caused by the different species of fungus might not vary. Special attention was paid to the rate of growth, the moisture requirements, and the effect upon the oil.

Our early observations confirmed Walker's [13] statement that two classes of plants known as bacteria and fungi are present and may be concerned in the deterioration of copra. Very early in the investigation we determined that bacteria normally play only a very minor rôle in the deterioration of copra, since a moisture content sufficiently high to favor bacterial growth is not found in ordinary copra. Therefore the investigation has not been concerned with the action of bacteria beyond a general confirmation of Walker's conclusions that bacteria grow only on fresh coconut meat or on copra, whose moisture is very high. Furthermore they cause little if any loss of oil even under conditions most favorable for their growth. Bacteria do seriously affect the appearance of the copra and the quality of the oil, as by their action they break the copra down into a slimy mass with an offensive odor. However, the fungi play a much more important part in the deterioration of the oil in copra than do bacteria.

Copra containing less than 20 per cent of water is practically free from bacterial action, and even above this moisture content the deterioration caused by fungi is of far greater importance. Not only are the moisture requirements of most of the fungi

[12] Op. cit., 117. [13] Op. cit. (1906), 1, 135.

with which we are concerned lower than those of the bacteria, but the fungi also cause a very considerable loss of oil and seriously impair its quality. They likewise injure the appearance of the product and help to collect dirt and other foreign material. If mold action is prevented, the action of bacteria is prevented at the same time and by the same methods.

The molds occurring upon copra belong to several groups of fungi, but they closely resemble each other in their vegetative habits and in their effect.[14]

We have found four molds constantly occurring upon moldy copra and coconut meat. The spore masses of these four molds differ greatly in color, and hence the molds are very readily distinguished even without the use of a microscope. In the order of the moisture necessary for their growth these molds are *Rhizopus* sp. (white mold), a mold occurring only upon fresh meat and there forming loose masses of white mycelium with many black sporangia; *Aspergillus niger* Van Tiegh. (black mold), a mold occurring on copra with a relatively high moisture content and producing black spore bodies which give the mold a black color; *Aspergillus flavus* Link (brown or yellow mold), a mold occurring most commonly on moldy copra. The spore masses are first greenish yellow, later turning brown; *Penicillium glaucum* Link (green mold), a mold producing green spore masses and common on copra, especially that containing a low percentage of moisture.

### RHIZOPUS SP. (WHITE MOLD)

*Rhizopus* occurs only upon fresh coconut meat and then only when the surrounding air is in a practically saturated condition. When moisture conditions are favorable, the growth of this mold is very luxuriant. It spreads by means of stolons, and in from thirty-six to forty-eight hours the mycelium frequently entirely

[14] Molds grow from extremely minute single-celled bodies called spores, which correspond to seeds in the higher plants. When a spore of one of these fungi germinates, it puts forth one or more delicate, colorless filaments, which grow in length, branch repeatedly, and work their way through the coconut meat or the copra. At the time this thread is growing, it is breaking down the oil and cell walls of the coconut by means of enzymes, is using the material to build up its own tissue, and is liberating in the process carbon dioxide and water. When the fungus fruits or produces spores, the plant itself becomes visible to the observer. We should remember when considering mold action that the part active in the destruction of the oil is invisible and that it is active in this destruction almost from the moment the spore germinates, which takes place some time before the fungus becomes visible.

covers a piece of coconut meat 10 centimeters in diameter with a tangled mass of aërial mycelium, which may attain a height of from 3 to 5 centimeters and which is specked with small black sporangia. The aërial mycelium collapses upon the slightest drying. The spores germinate in about six hours in a hanging drop of coconut decoction. Although this mold grows rapidly and destroys a high percentage of the oil in the meat, it is probably the least important of the four molds considered in this paper. It grows only upon fresh meat, and hence its growth is checked and the plant killed almost as soon as drying commences. *Rhizopus* can rarely make any considerable growth, since the meat is usually treated or placed on the grate and heat applied within the period necessary for the germination of the spore.

*Morphology.*—Mycelium hyaline, young hyphæ clear, older ones filled with granular material. Filaments about 8 $\mu$ in diameter. Sporophores arising in groups of two or three; stalk about 0.8 to 1 millimeter in height, 10 $\mu$ in diameter. Sporangium 100 to 140 $\mu$ in diameter, first globular, the wall later rupturing and folding back. Spores black in mass. The single spore brownish, smooth, 7 to 9 by 4 to 5 $\mu$.

*Oil loss caused by Rhizopus sp. (white mold).*—Table VII shows the oil loss due to white mold acting upon grated coconut meat in a saturated atmosphere during a period of about ten days. The experiment was performed and the oil loss calculated as follows: Freshly grated meat from one coconut was divided into several samples of approximately 10 grams each and accurately weighed into separate tared extraction thimbles. The original total oil of the several samples was calculated from the average analysis of two of the samples, and the remaining tubes and contents were sterilized and inoculated with spores of *Rhizopus* sp. After the mold had been allowed to act for a period of ten days, the thimbles were extracted with chloroform, and the loss in oil was calculated from the original total oil content and the total oil remaining after mold action.

TABLE VII.—*Oil loss due to the action of Rhizopus (white mold).*

| Sample No. | Weight of copra. | Total oil in copra. | | Loss of oil. | | Acidity as oleic. |
|---|---|---|---|---|---|---|
| | | Before mold action. | After mold action. | | | |
| | *g.* | *g.* | *g.* | *g.* | *Per cent.* | *Per cent.* |
| 1 | 4.7734 | 1.4749 | 0.8392 | 0.6357 | 43.1 | 21.0 |
| 2 | 6.1445 | 1.8986 | 1.2060 | 0.6926 | 36.4 | 19.8 |
| 3 | 6.3562 | 1.9646 | 1.1582 | 0.8057 | 41.0 | 26.6 |

The conditions under which the mold acted were the most favorable possible. The coconut meat was kept in a saturated atmosphere. The meat was grated, and therefore a greater surface was exposed to mold action than is the case in ungrated meat. Undoubtedly the loss in oil was higher than is to be expected under ordinary conditions. The table is of value also in showing that this mold under favorable conditions does destroy a very high percentage of the oil in the meat and that oil from such meat has a high percentage of free acid.

Grated meat was used to overcome certain difficulties in manipulation that arose in attempting to discover the oil loss due to this mold in ungrated meat. It was found possible more easily to prevent bacterial growth in grated meat. In ungrated meat bacteria soon appear on the surface and change it into a slimy mass upon which molds do not grow.

It is impossible to shred or grind ungrated meat after the mold has grown upon it so that complete extraction of the oil is possible without a change in the oil content, due to losing meat and oil on the grater and thus rendering the results worthless for comparison. The noting of the total oil content before and after mold action is necessary in order to give the true oil loss.

### ASPERGILLUS NIGER VAN TIEGH. (BLACK MOLD)

This species of *Aspergillus* plays a more important part than does *Rhizopus* sp., but a far less important one than does *Aspergillus flavus* (brown mold). It is the black mold often seen on badly molded copra. Its moisture requirements are lower than those of white mold, but slightly higher than those of brown mold, and although it often grows with the latter, it appears only upon copra that contains at least 12 per cent of water, and it makes its most luxuriant growth upon copra that contains 18 to 20 per cent of water. Properly dried copra should not have such a high moisture content as is required for the growth of this mold. However, as copra is usually prepared in the Philippines, it often contains enough water for this mold to appear and to make a considerable growth, and under such conditions it undoubtedly causes an appreciable loss in oil. Our experiments indicate that this loss may sometimes be as much as 40 per cent of the total oil.

In hanging drops the spores germinate in about six hours, and the subsequent growth is rapid. In forty-eight hours the mycelium from a single spore may grow out and extend over an area from 3 to 4 centimeters in diameter. On a nutrient agar medium such as coconut, prune, or string bean the colonies are

circular in outline and the substratum is yellow. This color is also often seen when the mold grows upon coconut or copra, and it appears to be characteristic of the species.

*Morphology.*—Hyphæ hyaline, 3 to 8 $\mu$ in diameter. Stalk of conidiophore erect, unbranched, 2 to 3 millimeters in height. Head 140 to 160 $\mu$ in diameter. Swollen tip of conidiophore 70 to 80 $\mu$ in diameter. Spores in chains radiating in all directions from the tip of the conidiophore. Spores first brownish, later black, globular, smooth, 4 to 5 $\mu$ in diameter.

*Oil loss caused by Aspergillus niger (black mold).*—Table VIII shows the loss in oil due to the action of this mold upon grated copra in a saturated atmosphere during a period of about ten days. The experiment was performed and the results calculated after the method already described under *Rhizopus.*

TABLE VIII.—*Oil loss due to the action of Aspergillus niger (black mold).*

| Sample No. | Weight of copra. | Weight of oil in copra. | | Loss of oil.[a] | | Acidity as oleic. |
|---|---|---|---|---|---|---|
| | | Before mold action. | After mold action. | | | |
| | *g.* | *g.* | *g.* | *g.* | *Per cent.* | *Per cent.* |
| 1 | 5.8335 | 1.8025 | 0.8778 | 0.9247 | 51.3 | 9.5 |
| 2 | 5.1663 | 1.5962 | 1.2282 | 0.3680 | 23.0 | 8.0 |
| 3 | 5.5930 | 1.7282 | 1.5019 | 0.2263 | 13.0 | 2.9 |

[a] The wide variation in per cent of oil loss is due to the extent of the mold growth; for example, in the case of sample 1 the meat was covered with a most luxuriant growth, while in sample 3 the mold developed a much smaller growth.

The oil loss varies somewhat in the three samples considered, but all show that there is a marked loss of oil under conditions favorable for mold growth. The amount of acid in the oil produced is too high for the oil to be considered good, but it is rather low in comparison with that produced by the brown and the white molds.

### ASPERGILLUS FLAVUS LINK (BROWN MOLD)

This species of *Aspergillus* is the mold that plays the most important part in the destruction of the oil in copra. It is the brown mold that is usually seen on badly molded copra. In many cases it is mixed with the black *Aspergillus* discussed above and often with the green *Penicillium,* which is considered later. It occurs upon copra with a moisture content of from 7 to 8 per cent—a water content lower than the average for Philippine copra—and because of its ability to grow on copra with so low a moisture content, it destroys a very high percentage of the copra

of the Islands. The oil destroyed may be almost 40 per cent of the total oil contained in the copra. The oil expressed from copra upon which this mold has been growing also contains a high percentage of free fatty acid.

In hanging drops the spores germinate in from four to five hours. In nutrient agar media the mycelium becomes visible in from twelve to fifteen hours and mature spores are produced in about forty-eight hours. The growth from a single spore is slow as compared with one of white mold or black mold, but the early production of spores leads to a rapid multiplication of colonies, and so the mold in a comparatively short time will completely cover the surface of the meat of half a coconut.

*Oil loss caused by Aspergillus flavus (brown mold).*—Table IX shows the loss of oil due to brown mold growing upon pieces of copra for one month. The experiment was performed and the oil loss calculated as follows: Pieces of copra with about 8 per cent moisture content were weighed, placed in a closed container so the amount of moisture in the air could be kept under control, and were inoculated with spores of brown mold. The total oil content of the copra was determined by the analysis of other pieces taken from the same nut. After the mold had grown for thirty days, the copra was removed and analyzed. The difference between the two analyses gives the loss in oil due to the action of the brown mold. At the completion of the experiment the pieces upon which the mold had grown were covered with a dense layer of brown mold from 4 to 7 millimeters thick. When broken open, the meat for about one half to two thirds the thickness of the piece was light in color, dry and fibrous, and in every way the same in appearance as commercial copra damaged by this fungus.

TABLE IX.—*Oil loss due to the action of Aspergillus flavus (brown mold).*

| Sample No. | Weight of copra. | Total oil. | | Loss of oil. | | Acidity as oleic acid. | |
|---|---|---|---|---|---|---|---|
| | | Original. | After one month. | | | Original. | After one month. |
| | *g.* | *g.* | *g.* | *g.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 15.57 | 9.1645 | 6.3465 | 2.8180 | 30.7 | 0.9 | 6.8 |
| 2 | 13.51 | 7.9540 | 5.5846 | 2.3694 | 29.8 | 0.9 | 5.1 |
| 3 | 14.83 | 8.8386 | 5.8570 | 2.9816 | 33.7 | 0.56 | 7.7 |
| 4 | 18.13 | 10.8055 | 6.7880 | 4.0175 | 37.2 | 0.56 | 7.2 |
| 5 | 14.89 | 8.8744 | 5.6010 | 3.2734 | 36.8 | 0.56 | 6.5 |
| 6 | 13.71 | 8.1969 | 5.1610 | 3.0359 | 37.0 | 0.7 | 7.0 |
| 7[a] | 11.69 | 6.7334 | 5.3245 | 1.4089 | 20.9 | 0.7 | 5.8 |
| 8 | 11.66 | 6.7161 | 4.0076 | 2.7091 | 40.3 | 0.7 | 9.1 |

[a] Removed before the end of thirty days.

The destruction of oil caused by this mold acting for a period of one month under favorable conditions is found to be from about 30 to 40 per cent of the total oil contained in anhydrous copra, while there is a very considerable production of free fatty acid, which shows the deterioration in quality of the oil remaining. As this mold may occur on copra with a fairly small water content, a large part of the Philippine copra is subject to its attack. Under favorable conditions it may destroy as much as 40 per cent of the oil. Since the probable loss caused by brown mold averages nearly 25 per cent, it is evident that the loss to the Philippines from this cause alone equals a very considerable portion of the value of the copra exported.

PENICILLIUM GLAUCUM LINK (GREEN MOLD)

This is the common green mold often seen upon copra. It grows well on copra containing a very low percentage of water. Analyses show that this mold destroys hardly any of the oil in the copra, and the production of free acid is low; therefore a good grade of oil can be made from copra upon which this mold has growth. Its growth appears to be almost entirely superficial. It can be readily removed by brushing, leaving a firm white copra. A growth of *Penicillium* alone may be said almost to serve as an indicator of good copra, because it grows at a moisture content between 5 and 7 per cent, causes practically no loss in the oil content, and produces very little free acid. However, green mold growing with one or both of the species of *Aspergillus* loses its significance as an indicator of good copra, as it will grow at any degree of moisture higher than 5 or 6 per cent, and the *Aspergillus* indicates a high moisture content. The reason green mold does not usually appear upon copra with a high degree of moisture is because of its slow rate of growth. The spores germinate in hanging drops in about six and one-half hours, but the subsequent growth is slow, and colonies upon copra do not become visible to the naked eye until from about twenty-four to thirty-six hours after the spores are placed upon it. The colony grows very slowly, and mature colonies from a single spore are hardly ever more than 1 centimeter in diameter. The spores are mature in about eleven hours after the mycelium becomes visible. Due to the much more rapid growth of the other molds, *Penicillium* is either crowded out or covered over by them, and under high moisture conditions it is only after the other molds have stopped growing that *Penicillium* becomes visible.

*Oil loss caused by Penicillium (green mold) upon copra.*—Table X shows the effect of green mold upon the oil content of

copra and its production of free acid. Copra dried until it contained about 7 per cent water was inoculated with green mold and placed in a closed container in a moist atmosphere with which it was in equilibrium. After the mold had been allowed to grow for a period of thirty days, the copra was removed and analyzed.

TABLE X.—*Oil loss due to the action of Penicillium glaucum (green mold).*

| Sample No. | Weight of copra. | Total oil. Before mold action. | Total oil. After mold action. | Loss of oil. | Loss of oil. | Acidity as oleic acid. Original. | Acidity as oleic acid. After mold action. |
|---|---|---|---|---|---|---|---|
| | *g.* | *g.* | *g.* | *g.* | *P. ct.* | *P. ct.* | *P. ct.* |
| 1 | 13.07 | 7.3192 | 7.3040 | 0.0152 | 0.20 | 0.79 | 1.2 |
| 2 | 14.16 | 7.9296 | 7.8823 | 0.0473 | 0.69 | 0.79 | 1.0 |
| 3 | 10.04 | 5.6224 | 5.5731 | 0.0492 | 0.87 | 0.79 | 0.9 |
| 4 | 13.34 | 7.4704 | 7.4306 | 0.0404 | 0.54 | 0.79 | 0.75 |

Table X shows that green mold growing under the most favorable conditions during one month causes an almost negligible loss of oil and that the production of free acid is extremely low.

At the end of the experiment the pieces of copra were covered with a dense mass of green mold about 5.5 millimeters in thickness, but when this was removed by brushing, the copra beneath was firm and white with no evidence of penetration by the mold.

### SUMMARY OF OIL LOSS AND DETERIORATION CAUSED BY MOLDS

Table XI, which summarizes the results secured in the experiments upon oil loss and production of free acid, is included in order more easily to compare the loss in quantity and injury to the quality of the oil caused by the four principal molds occurring upon copra.

Table XI shows that the copra dealer may expect a loss of from 30 to 40 per cent upon all copra which contains sufficient water to enable brown mold to grow; a further increase of the water content makes very little difference, as brown mold will then grow with black mold and raise the oil loss to that caused by brown mold alone. The loss in quantity and quality of oil is always in addition to the loss suffered by the purchase of water at the price of copra. Where green mold alone is present, there is little loss in oil. However, the presence of this mold indicates a copra with a higher water content than where no mold is present; if such copra is stored where the air is in a practically saturated condition, it will absorb enough water for brown mold to attack it much sooner than will clean copra.

TABLE XI.—*Summary showing effect of mold action on the quantity and free acidity of oil in copra.*

[The critical moisture content for the growth of each mold is given under the special headings.]

| Sample No. | Mold acting for 10 days upon shredded meat. | | | | Mold acting for 30 days upon unshredded copra. | | | |
|---|---|---|---|---|---|---|---|---|
| | White mold (*Rhizopus sp.*) | | Black mold (*Aspergillus niger*). | | Brown mold (*Aspergillus flavus*). | | Green mold (*Penecillium glaucum*). | |
| | Oil loss. | Free acid as oleic. | Oil loss. | Free acid as oleic. | Oil loss. | Free acid as oleic. | Oil loss. | Free acid as oleic. |
| | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 43.1 | 21.0 | 51.3 | 9.5 | 30.7 | 6.8 | 6.20 | 1.2 |
| 2 | 36.4 | 19.8 | 23.0 | 8.0 | 29.8 | 5.1 | 0.69 | 1.0 |
| 3 | 41.0 | 26.6 | 13.0 | 2.9 | 33.7 | 7.7 | 0.87 | 0.9 |
| 4 | | | | | 37.2 | 7.2 | 0.54 | 0.8 |
| 5 | | | | | 36.8 | 6.5 | | |
| 6 | | | | | 37.0 | 7.0 | | |
| 7 | | | | | 40.3 | 9.1 | | |
| Average | 40.2 | 22.5 | 29.1 | 6.8 | 35.1 | 7.1 | 0.6 | 1.0 |

In the experiments to determine the critical moisture content of copra for the growth of the various microörganisms, we found uneven distribution of water within a given piece of copra. The total water content may be as low as 5 per cent, sufficiently dry to prohibit mold growth, while the upper portion of the meat may be practically saturated. For clearness and convenience the terms upper and lower layer will be used in the following discussion. By the upper layer is meant that portion of the meat beginning at the surface of the meat adjacent to the water portion of the coconut and extending outward approximately to one fifth of the thickness of the meat; the lower layer is the remainder of the meat. The moisture content of the upper layer is more important in relationship to mold growth than the total water content of the sample, because this portion is first attacked. It is impossible to obtain exact data as to the water content necessary for mold growth, because of the difficulty of obtaining a uniform sample of the upper layer. In Table XII the figures are approximate values for the moisture content of the separate layers.

In every case the percentage of water in the upper layer is much higher than in the lower layer or in the general sample and is high enough to support the growth of the more destructive molds. The percentage of water based on the general sample would lead one to believe this to be a well-dried copra that would be resistant to mold attack.

TABLE XII.—*Moisture content of the upper and the lower layers of general samples of copra after storage in a moist atmosphere.*

| Sample No. | Weight of— | | Water in— | | |
|---|---|---|---|---|---|
| | Upper layer. | Lower layer. | Upper layer. | Lower layer. | General sample. |
| | *g.* | *g.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 14.7681 | 65.7966 | 13.36 | 6.4 | 7.6 |
| 2 | 3.5100 | 43.8112 | 21.52 | 7.8 | 8.8 |
| 3 | 5.5798 | 30.2842 | 20.43 | 8.9 | 10.7 |
| 4 | 14.1452 | 32.1548 | 11.3 | 6.5 | 8.0 |
| 5 | 12.8122 | 26.5142 | 24.0 | 6.8 | 12.5 |
| 6 | 10.2004 | 23.7875 | 10.9 | 5.7 | 7.9 |
| 7 | 11.0936 | 29.2013 | 10.5 | 7.6 | 8.4 |

## HEAT AND ITS RELATION TO MOLD GROWTH

While investigating the rise of temperature occurring in moldy copra when piled in large quantities, it was noticed that the temperature increases to a certain maximum of about 50° C. and then declines. As this rise in temperature appeared to be related to mold action, the question presented itself whether the fall after attaining a maximum might to be due to the fact that such temperatures inhibit the growth or kill the mold concerned. It is well known that temperatures around 50° C. will, when long maintained, kill the mycelium of many species of fungi or at least stop their growth. In general, the spores of fungi are more resistant to heat than the mycelium and so might survive such temperatures. However, in this case there was no recurrence of a high temperature, as might have been expected had spores of the fungi survived and, after the temperature decline, returned to normal germination and resumed their growth. To determine the effect of such temperature upon the spores and mycelium of the four molds considered in this paper, the following experiments were conducted:

Molds in pure culture were allowed to grow until a mycelium was distinctly visible and then were placed in an oven maintained at a constant temperature of 50° C. At intervals cultures were removed from the oven and kept at room temperature to see whether growth was resumed. To determine the effect of this temperature upon mold spores, pieces of coconut meat were inoculated with mold spores, put in closed containers, and placed in the oven. At intervals pieces of the meat were removed and kept at room temperatures to determine whether germination occurred. The observations from these two series of experiments indicate that both the spores and the mycelium of each

of the molds survive a temperature of 50° C. for from nine to twelve hours, since removal from the oven permitted both germination and growth to proceed at the normal rate.

### ABSORPTION OF WATER BY COPRA

The question may be asked, will copra once thoroughly dried absorb enough moisture from the atmosphere during storage to raise its moisture content to a point where molds may grow? Should this occur, what is the use of thorough drying, if during subsequent storage and shipment mold will gain a foothold and destroy a high percentage of the oil and impair the quality of the remainder? This is a most important question from the point of view of the copra dealer, and in order to formulate an answer, a number of variable factors must be taken into consideration.

Generally speaking, it has been our experience that when dried to a moisture content of about 6 per cent copra does not mold when stored where there is a circulation of air. However, when kept in a saturated atmosphere, it will eventually absorb enough water to enable mold to grow, but this only takes place after it has been exposed to such conditions for from one to two weeks. It would probably very rarely happen that the air in a warehouse or in the hold of a ship will reach a point of saturation and, if this does occur, that the humidity will be replenished when it is absorbed by the copra and that these conditions will last for so long a period even as one week. Copra which has been dried only to about 7.5 per cent of moisture often will not grow mold in the open air probably because the surface is really dried out below this moisture content, but when stored under the same conditions as above, will develop mold in from two to five days.

Another factor which has an influence is the rôle played by the water liberated during the processes of metabolism of the mold. Mold grows at the expense of the oil and fiber of the copra, converting them into water and carbon dioxide. If the lower part of a large pile of copra contains sufficient water to permit molds to grow, the whole may mold, due to the water that is liberated during mold growth being confined in the pile long enough for the remainder of the copra to absorb enough moisture in turn to support mold growth.

All of our experiments tend to show that copra once properly dried to approximately 6 per cent moisture does not absorb sufficient water, unless in a saturated atmosphere for prolonged periods of time, to develop even a superficial growth of mold.

In Table XIII weighed pieces of copra were kept in a saturated atmosphere at room temperature with daily weights recorded until mold growth appeared.

TABLE XIII.—*Change in moisture content of copra stored in saturated atmosphere (at 29° C.) until mold appeared.*

| Days. | Gain in weight of sample— | | | |
|---|---|---|---|---|
| | I. | II. | III. | IV. |
| | g. | g. | g. | g. |
| 1 | 0.94 | 0.24 | | |
| 2 | 1.26 | 0.71 | 0.88 | 0.80 |
| 3 | | | 1.82 | 1.98 |
| 5 | 3.14 | 2.13 | 2.18 | 2.25 |
| 6 | 3.64 | 2.61 | 2.19 | 2.30 |
| 7 | 4.24 | 3.20 | 2.41 | 2.87 |
| 8 | 4.48 | 3.28 | 2.49 | 2.73 |
| 9 | | 3.91 | | |
| 10 | | 4.05 | 2.69 | 3.19 |
| 12 | | 4.55 | | |
| Original weight grams | 83.51 | 92.76 | 64.50 | 85.99 |
| Total increase in weight per cent | 5.3 | 4.9 | 4.2 | 3.7 |
| Original total water do | 2.6 | 3.4 | 3.9 | 5.0 |
| End total water do | 7.6 | 8.0 | 7.9 | 8.4 |

In one case mold appeared on the eighth day, in two on the tenth, and in the remaining one on the twelfth.

TABLE XIV.—*Change in weight of copra stored in open air at atmosphere temperature.*

| Days. | Relative humidity in Manila on day weighed.[a] | Change in weight of sample—[b] | | | | |
|---|---|---|---|---|---|---|
| | | I. | II. | III. | IV. | V. |
| | | g. | g. | g. | g. | g. |
| 1 | 91 | +0.13 | 0.22 | +0.10 | +0.07 | +0.02 |
| 3 | 98.5 | 0.02 | 0.85 | +0.11 | +0.07 | +0.02 |
| 7 | 94.5 | 0.35 | 1.45 | 0.11 | 0.13 | 0.22 |
| 11 | 73.5 | 0.35 | 1.44 | 0.07 | 0.13 | 0.21 |
| 16 | 94.2 | 0.37 | 1.81 | 0.16 | 0.18 | 0.33 |
| 38 | 88.6 | 0.47 | 2.13 | 0.16 | 0.24 | 0.45 |
| 46 | 85.9 | 0.37 | 1.90 | 0.12 | 0.18 | 0.10 |
| Total loss per cent | | 1.2 | 6.0 | 0.47 | 0.76 | 0.40 |
| Original total water do | | 6.8 | 11.7 | 5.37 | 5.66 | 6.70 |
| End total water do | | 5.6 | 5.7 | 4.9 | 4.9 | 6.3 |
| Original copra weight grams | | 29.75 | 31.53 | 25.35 | 23.93 | 24.89 |
| End upper portion water per cent | | 9.4 | 8.8 | 9.0 | 8.7 | 9.1 |
| End lower portion water do | | 4.5 | 5.0 | 3.8 | 3.8 | 5.4 |

[a] Algué, José. Weather Bureau Bulletins for June and July (1916).

[b] This is marked +, where an increase in weight resulted, but no mark is used where this change was a decrease.

In Table XIV are recorded data relative to weighed pieces of copra kept in the open. The weight in grams is recorded under series number of samples.

At the end of fifty-six days no mold growth had formed. The last ten days were a period of wet weather, during which moisture was absorbed by the upper portion of the meat as shown by comparison of the upper and lower portions. This change of moisture content of the upper layer when calculated on the total weight shows a relatively small change in the percentage moisture. From this it is seen that copra stored in the open air will lose or gain water until it is in equilibrium with the atmospheric moisture. This equilibrium point is about 5 per cent moisture for copra.

The copra in Table XIII had developed a fair growth of mold by the end of two weeks. There are only short periods during the rainy season when the air is practically saturated with moisture, and unless dry copra were stored in containers in a saturated atmosphere, no molding would take place. It will be noticed that the total moisture content of each piece is extremely low, but if, on the other hand, copra containing from 7 per cent to the amount of moisture contained in fresh meat had been stored under like conditions, the mold would have practically destroyed the copra in the course of several days. This would also be the case if copra of 7 per cent or more was stored without air circulation, the damage due to mold depending upon the moisture present. In Table XV data on good quality of machine-dried copra without mold, stored in five sacks, are recorded. Temperature readings of the copra and outside atmosphere were noted from time to time. Weights of the lot before and after were not recorded, as insects destroyed a part of the copra.

Table XV indicates no temperature change where no deterioration of meat and oil occurs and, further, that copra once properly dried does not develop mold when stored.

Copra which has been machine-dried and not cooled before being placed in a large pile becomes hot and later often shows mold growth. We believe this to arise from a breaking down of oil and cellular matter from heating (the heating is similar in character to the spontaneous heating of oily rags) into carbon dioxide and water vapor. The moisture of the surface of the copra is raised in this manner to a point where it will support mold growth, and thus microörganisms appear. The temperature at which the copra is stored is a factor in this heating. When the copra is carefully cooled, the oxidation at the lower temperature is so slow that no appreciable heat is given off and

it escapes without any rise in the temperature of the pile. The theory of some of the copra men that the moisture content of the copra is increased by the condensation of moisture from the cool air surrounding the warm copra is absolutely untenable.

TABLE XV.—*Data on machine-dried copra stored in sacks.*

| Date. | Sample. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I. | | II. | | III. | | IV. | | V. | |
| | Copra. | Air. | Copra. | Air. | Copra. | Air. | Copra. | Air. | Copra. | Air. |
| | °C. | °C. | °C. | °C. | °C. | °C. | °C. | °C. | °C. | °C. |
| March 20 | 31 | 31 | 30 | 30 | 29.5 | 29.5 | 30 | 30 | 30.5 | 30.5 |
| April 1 | 30 | 30.5 | 29 | 30 | 29.0 | 29.0 | 30.5 | 30 | 31.0 | 31.0 |
| April 11 | 30 | 30.5 | 28 | 29.5 | 30.5 | 30.0 | 29.5 | 30 | 29.5 | 30.0 |
| April 20 | 31 | 30.5 | 29 | 29 | 31.0 | 31.0 | 32.0 | 32.5 | 32 | 32.0 |
| May 1 | 32 | 31.5 | 29 | 29.5 | 30.5 | 31 | 29.1 | 28.5 | 32 | 31.0 |
| May 15 | 32 | 31.5 | 29 | 29.5 | 31 | 30.5 | 31.5 | 31.5 | 32.4 | 31.3 |
| Original water ... P. ct. | [a]6.1 | | | | | | | | | |
| Water May 15 ... do | 4.9 | | 5.9 | | 4.8 | | 4.1 | | 4.1 | |

[a] Moisture content of a general sample made up of I, II, III, IV, and V.

## COPRA-DRYING METHODS IN USE

The poor quality of Philippine copra due to insufficient drying and improper handling is, of course, dependent upon the methods employed. There are two general methods in use in the Islands, sundrying and kiln drying; improvement of both is possible to a certain extent. The sundrying method used throughout the southern islands produces the better grade of copra; it consists simply in halving the nuts, without previously husking, and exposing the meat to the sun. Where sufficient care is exercised in the way of cleanliness and complete drying, the method produces an excellent grade of copra.

The periods of daily rains do not favor this process in parts of the Philippine Islands, and there the grill method is used. In the grill, or tapahan, process the nuts are husked, halved, and placed on bamboo mats, under which shells and husks are burned.[15] After the meat is partially dry, it is removed from the the shells and is subjected to further drying. Analyses show that the finished product as it leaves the dryer contains at least 20 per cent moisture.

[15] For more complete description of sundrying and grill methods, see Pratt, D. S., *This Journal, Sec. A* (1914), 9, 177.

TABLE XVI.—*Water content of tapahan-dried copra.*

| Sample No. | Moisture. Per cent. |
|---|---|
| 1 | 21.57 |
| 2 | 25.57 |
| 3 | 28.77 |
| 4 | 25.98 |
| 5 | 20.52 |
| 6 | 25.54 |
| 7 | 28.51 |

The samples noted in Table XVI were obtained from the copra from seven tapahans at the completion of the drying process. The very high moisture percentage indicates imperfect drying, a condition most favorable for mold growth and bacterial action with the attending deterioration of the copra. After the first handling and drying to only approximately one half the original moisture contents, these samples were dirty and smoky in appearance. Complete drying by the tapahan method, a proceeding probably never carried out in practice by the producers, requires about four days and gives a very badly smoked product. The uneven heating obtained on the tapahan is a bad feature of the method in that the pieces directly in contact with the grill are overheated and dry much more rapidly than the upper layers. This is especially true in cases where the half nuts are piled up several layers deep. The tapahan is so constructed that it favors uneven drying and much smoking of the copra. It consists of a pit, dug in the ground to the depth of 3 meters, connected at the bottom by a narrow underground tunnel to the heat chamber. The heat chamber is approximately 2 meters wide and 6 meters long, the dimensions varying, with the bottom sloping down to meet the tunnel. It is covered with a plaited mat of bamboo or rattan, or in some cases with stripes of split bamboo, upon which the half nuts are piled. Shells, and sometimes husks as well, are burned in the bottom of the pit, the heat and smoke passing through the pile of copra. An attempt was made to improve a "tapahan" by providing it with a chimney and a special fire box. By burning only shells, much of the smoke was eliminated, but the copra was unevenly dried.

Even with these two existing methods a better grade of copra could be prepared than is now the case in the Philippines if proper care were exercised in handling the product. By using sundrying in conjunction with the tapahan, a more evenly dried product could be obtained. In the southern islands, where the drying could be carried on entirely by the sun's heat, the precautions necessary would be to keep the copra free from

dirt and to secure more complete drying with facilities to protect it during short rainy periods. Pratt [16] states that copra produced in other countries by like means commands a higher price than Philippine copra and must be considered as superior in the world's market.

### MECHANICAL DRYERS

Mechanical dryers are one possible solution of the problem for improving the copra production of the Islands, but they have not been introduced in a commercial way. Several machines have originated in the Philippines that require considerable handling of the meat, but while their product is of good quality, initial and operating expenses seem to be too great to warrant their adoption. Smith [17] gives descriptions and drawings of several types of drying machines. At two of the copra-oil mills here large hot-air dryers have been installed for redrying copra before it is milled. This apparatus, with changes, might be adapted to the drying of fresh meat. It has the advantage over other forms of dryers in being a continuous process with the minimum amount of handling of the product. A small cheaply constructed dryer, combining low operating expenses and rapid drying, would find a ready market in the Philippines.

Mechanical drying machines have been discredited by the public through the belief that when coconut meat is dried in a current of hot air a part of the oil is carried away from the copra. This supposition is not in accord with what one might expect from a study of the physical properties of coconut oil. It was found that when coconut oil was heated for four hours in a current of hot air at 100° C. there was no appreciable loss in weight.

Pure coconut oil was dried in vacuum over sulphuric acid for four days, after which it was heated in an oven at 100° C. for four hours with the following results:

TABLE XVII.—*Loss on heating coconut oil at 100° C. for four hours.*

| Oil No. | Weight of oil. | Weight lost. |
|---|---|---|
| | *g.* | *Per cent.* |
| I | 4.9112 | 0.022 |
| II | 4.8919 | 0.024 |
| III | 3.9282 | 0.022 |
| IV | 4.7955 | 0.023 |

[16] Op. cit.

[17] Smith, H. Hammel, Coconuts. The Consols of the East. Tropical Life, London (1913).

However, it did appear possible that there might be a mechanical carrying over of the oil with the escaping moisture, especially if the drying temperature were high and the driving off of moisture rapid. Experiments were made by examination of the gases from a mechanical dryer. The type of machine used was similar to the ordinary oven dryer, but provided with an arrangement for the circulation of hot air. The experiment was carried out in the following manner:

A weighed amount of coconut meat was distributed over the trays and dried at various temperatures. The volume of air passing through was calculated, and the temperatures at the entrance and exhaust were noted. An aliquot part of the air was withdrawn from the oven by means of a vacuum pump at the rate of 1,200 liters per hour, measured by means of a gas meter. The air in passing to the pump and gas meter was conducted through two series of four bottles, each containing chloroform immersed in a freezing solution in order to free the air of oil. Four separate determinations were made, using drying temperatures varying from 70° to 100° C., and in no case was a qualitative test for oil obtained.

TABLE XVIII.—*Data on oil loss in mechanical dryer.*

| | Temperature. | Fresh meat. | Weight loss. | Oil loss. |
|---|---|---|---|---|
| | °*C.* | *Kilos.* | *P. cent.* | *Per cent.* |
| Determination 1 | 70 | 100 | 40.0 | 0.0 |
| Determination 2 | 80 | 104 | 42.0 | 0.0 |
| Determination 3 | 90 | 102 | 41.0 | 0.0 |
| Determination 4 | 100 | 96 | 44.0 | 0.0 |

The results recorded in Table XVIII are opposite to the belief of the Ceylon planters, as reported by Pratt: [18]

The amount of copra from a given quantity of fresh nuts depends to a considerable extent upon the rate of artificial drying. Ordinarily, from 170 to 200 nuts give about 50 kilograms (110 pounds) of copra. The two extremes are encountered in comparing the output of sundried copra with that of desiccated coconut products. * * * The decrease in time required for expelling the water is, therefore, coincident with increased loss of oil, and all methods of preparing copra must represent an economical balance between these factors. It is unquestionably possible to make copra in much less time than is required by either the sundrying or grill-drying processes, but experiments made by planters in Ceylon have not impressed them with the advisability of adopting such changes. One of the most progressive coconut planters in the island constructed a drying house with brick heating flues and produced paper-white copra in less than twenty-four

[18] Pratt, D. S., *This Journal, Sec. A* (1914), 9, 181.

hours, but discontinued the process because of the resulting high loss of oil. It is his opinion that a continuous slow current of air at from about 54° to 60° (130° to 140° F.)—the proper temperature to be determined by experiment—should complete the drying process within three days and nights, and with the least loss of oil. A rapid drying in ten hours must be attended by a considerable loss, and will require about 15 per cent more kernel to produce a given weight of copra.

With several of the statements in the above-quoted opinion we must take issue. Our experience proves that no oil loss occurs when rapid drying takes place at 80°, 90°, or 100° C. If by the ambiguous statement, "a considerable loss, and will require about 15 per cent more kernel to produce a given weight of copra," is meant anything other than more complete drying, the experience of the Ceylon planters is totally different from the results obtained in this investigation. As further evidence of the high yields of oil from desiccated coconut, Table XIX is appended. Did such losses of oil as reported by Pratt occur, the yields of oil in the copra recorded in this table would be much lower.

TABLE XIX.—*Data on drying copra under various conditions.*

| Sample No. | Means of drying. | Oil in anhydrous material. | Water. |
|---|---|---|---|
| | | *Per cent.* | *Per cent.* |
| 1 | Vacuum 80° C.; 14 centimeters; 9 hours | | |
| 2 | do | 74.10 | 6.4 |
| 3 | do | 70.7 | 7.3 |
| 4 | do | 71.3 | 7.1 |
| 5 | do | 73.7 | 4.0 |
| 6 | do | 69.1 | 5.2 |
| 7 | do | 72.9 | 3.9 |
| 8 | do | 68.0 | 4.7 |
| 9 | Hot air over 80° C.; 17 hours | 71.5 | 5.3 |
| 10 | do | 71.2 | .9 |
| 11 | do | 70.8 | 5.8 |
| 12 | do | 69.9 | 9.1 |
| 13 | Hot air over 90° C.; 17 hours | 72.2 | 5.4 |
| 15 | do | 68.5 | 5.1 |
| 16 | do | 69.0 | 7.5 |

PREPARING COPRA BY USE OF SULPHUR DIOXIDE

The Bureau of Science has developed a simple method for the preparation of copra by treatment with sulphur dioxide gas and

[a] Since perfecting this method we have noted the sulphur dioxide method of Marot (English patent 6379, 1906) described by Lewkowitsch in Chemical Technology and Analysis of Oils, Fats and Waxes. 5th ed. MacMillan & Co., London (1914), 2, 631.

allowing the meat to dry without the addition of artificial heat. The apparatus used is a wooden box, provided with trays with split bamboo bottoms, and a 4-wheel car consisting of framework and two pairs of small iron wheels mounted on a wooden track. The box is 1.05 by 2.10 by 2.70 meters and is provided with a door in one end, being of sufficient size to accommodate twelve trays separated sufficiently for free circulation of the gas and with a capacity for holding about 1,200 nuts. The track is twice the length of the box to facilitate loading and unloading of the car outside of the box. The operation is carried out in the following manner: The husked nuts are halved and spread on the trays with the concave side down, and the trays are loaded on the car and pushed into the box. Eight kilograms of sulphur are next placed in a shallow pit under the car and ignited. If the box is made comparatively tight, this amount of sulphur will burn for from ten to twelve hours, liberating sufficient sulphur dioxide gas for the treatment. At the end of the sulphuring period the car is rolled into the open and the meat is removed immediately from the shells with an ordinary copra knife, or is allowed to remain in the shells for from four to five days, at the end of which time the meat has become sufficiently dry to allow of its ready removal. In either case the sulphured material is spread out under cover with free access of air for a period of two weeks, after which it is cut up and sacked for the market. Obviously on sunny days spreading the meat in the open greatly hastens the drying and should be taken advantage of.

TABLE XX.—*Sulphur dioxide and water content of copra at various periods during the sulphur treatment.*[a]

| Hours treated. | Sulphur dioxide. | | | Water. | | | | |
|---|---|---|---|---|---|---|---|---|
| | Content immediately after treatment. | Content after 10 days. | Loss in total content during 10 days. | In fresh meat. | Immediately after treatment. | Loss in total, during treatment. | Ten days after treatment. | Loss in total, 10 days after treatment. |
| | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 6 | 0.1218 | 0.0412 | 66.2 | 47.7 | 42.2 | 14.2 | 13.1 | 73.1 |
| 9 | 0.1456 | 0.0425 | 70.8 | 46.1 | 41.7 | 15.5 | 12.6 | 72.9 |
| 13 | 0.1869 | 0.0672 | 64.1 | 49.2 | 37.2 | 27.0 | 13.7 | 73.0 |
| 18 | 0.2114 | 0.0722 | 65.9 | 48.9 | 39.0 | 23.0 | 11.1 | 81.1 |
| 24 | 0.3144 | 0.0715 | 77.3 | 48.5 | 45.5 | 15.9 | 8.0 | 82.1 |

[a] The maximum amount of sulphur dioxide that coconut meat will absorb was not determined. However, a twelve-hour continuous treatment with the gas was found to be sufficient in all cases.

The action of the sulphur dioxide on coconut meat serves a double purpose. The mold spores are destroyed, and a sufficient amount of the sulphur dioxide remains in the meat for the time necessary for the escape of the water to prevent the growth of new mold spores. Also, as will be shown in Table XX, there is a considerable loss of water during the treatment due to the softening of the cell walls from the action of the sulphur dioxide, which has a marked affinity for water.

Table XX shows data taken from analysis of sulphured coconut meat which was allowed to dry under cover. At no time was this meat exposed to the drying influence of the sun or artificial heat. The figures are averages from ten samples for each period of treatment and represent a close approximation of the true sulphur dioxide content.

The residual sulphur dioxide after one month's time may be disregarded, as only traces are found. A part of the samples from the series receiving six and nine hours sulphuring developed a slight growth of green mold which was entirely superficial, and after the meat was completely dry, it could be brushed off, leaving white copra exposed. Copra prepared by this method with treatments of twelve hours or more and if dried within two weeks is clean and white and free from mold, the oil expressed being practically colorless and free from rancidity and acidity. Sulphur dioxide was not detected in the expressed oil. It is pronounced equal to, or better than, the best Cochin oil and will, therefore, sell for from 4 to 6 centavos a pound more than the ordinary oil. At 4 centavos per pound this would mean an increased value of 3.28 pesos per picul of copra. With proper organization the labor cost by this method should not exceed that of the tapahan or sun-drying processes, and the initial outlay is small. Tarred paper may be substituted for wood in the construction of the box, and bamboo for the trays is inexpensive. Unless sundrying is used in conjunction, two weeks should elapse before marketing the copra, and while this time element is an objectionable factor, the increased value of the product would more than pay for the delay. The expense of sulphuring is also negligible when the superior quality of copra obtainable is considered. The sulphur need not be a refined grade; in fact the crude sulphur is preferable, as the impurities slacken the rate of combustion and, hence, increase the length of time of sulphuring from a given amount of sulphur. Sulphur is available in both the Philippines and Japan. A local demand would develop the sulphur resources of the Philippines; otherwise it could be imported from Japan more cheaply than is now the case with

Japan sulphur in the United States. In 1915 the United States Geological Survey[20] reports that during the calendar years 1911–14 Japan exported to the United States 16,185, 24,505, 15,317, and 21,913 tons of sulphur, respectively. If all of the nuts grown in the Philippines, approximately 431,387,000, were made into copra by the sulphur dioxide process, not more than 3,500 tons of sulphur would be required annually.

Pure coconut oil is water white and free from acidity and rancidity. It cannot be obtained from copra which has been acted upon by microörganisms. We would define good copra as coconut meat containing from 4 to 6 per cent water and 65 per cent oil, calculated on anhydrous meat, with an acid content of less than 1 per cent acid (oleic) and free from dirt and smoke. Such copra would find top prices on the world's market, and there is no reason why with time and improved methods Philippine copra could not be the world's standard rather than the poorest quality. The increased money value of such a product can be readily seen from a consideration of weight losses in storage and during shipment. Further the oil obtainable due to lack of necessity of purifying it from free fatty acids, rancidity, and color add materially to its value. The cost of refining commercial coconut oil is estimated at 8 pesos per each 1 per cent fatty acids per ton of oil.

Below are given comparative figures of market quotations for best-quality raw coconut oil and the ordinary commercial product.

TABLE XXI.—*Comparison of prices in pounds sterling per ton of various grades of coconut oil in the London market.*[a]

| Date. | Oil. | | |
|---|---|---|---|
| | Cochin. | Ceylon. | Commercial copra. |
| December 11, 1913 | 52–54 | 49–51 | 45–51 |
| December 11, 1914 | 60 | 50 | 46–49 |
| November 20, 1915 | 51–53 | 49–51 | 38–48 |

[a] *Tropical Life* (Dec., 1915), 236.

## FURTHER SUGGESTION FOR THE IMPROVEMENT OF COPRA

Ripe nuts only should be used for the production of copra, because only fully matured nuts produce copra containing the maximum oil content.[21] The practice of picking green nuts in the

[20] Cox, Alvin J., *Bureau of Science Press Bull.* (1916), No. 54.
[21] See Walker, H. S., *This Journal* (1906), 1, 58.

Philippines in order to take advantage of market fluctuations is well known, and sorting out the "mulos"—rubbery pieces of unripe meat, which will not become dry—is a recognized part of the copra industry. Aside from its low oil content, green copra must be worked separately; consequently the presence of green copra interferes with the routine of the mill and increases the cost of handling. In some coconut-producing countries laws are or have been in effect prohibiting the picking of coconuts.[22] Such a law is impracticable in the Philippine Islands, since certain kinds of coconuts here do not drop their fruit until they have become much overripe. In order to make it practicable to find and collect nuts which have fallen from the tree, clean cultural methods should be practiced on the plantation by burning the taller weeds and dead wood. By such methods of culture not only is the soil fertilized to a certain extent by the ash and decaying vegetation, but also the breeding places of many of the insects and fungi which prey upon the coconut are destroyed, so that the health of the trees is improved and ultimately the production of nuts increased.

The nuts when opened should be kept free from dirt and dried immediately and without smoking to a water content of 5 per cent.

The establishment of copra standards and organization of copra centrals by the Government has been proposed. The Bureau of Science has for some time had the problem of classification of copra under consideration. In view of the large number of classes necessary to meet the requirements due to the several factors—oil content, moisture, acidity, and appearance of the copra—complete standardization would be difficult to establish.

Under the present conditions a consignment of copra received from the provinces at the Manila bodegas may represent the product of 100 or more different producers, which means that practically no two sacks have been dried to the same moisture content. And aside from the necessity of analyzing a sample from each sack, the fact that uneven drying has been practiced and that the variation of the several factors in each nut is considerable, the analysis would be at best a rough approximation. The classification of copra under chemical control would be possible in conjunction with a system of inspection, as is practiced in hemp grading. It requires experience in order only to tell if a piece of copra is dry. In the hands of honest and competent

[22] Pratt, D. S., op. cit., 179.

inspectors stationed at the various shipping centers in the provinces a uniform product only would be marketed, and under this condition chemical analysis would be a valuable means of determining the worth of a parcel of copra.

The probable solution of the copra problem will come through educational measures and encouragement of the investment of capital in coconut plantations. Modern plantation managers will apply improved methods, and the small grower will necessarily follow their example or be satisfied with a discriminating price for his poorer quality of copra. At present the Manila market does not demand a high grade of copra. Any quality of copra sells and with too little difference in price from the best grade. The ordinary dealers are satisfied to make their profit on poor grades of copra. At present a poor grade of copra controls the market; in fact no other is available in large quantities, and parcels of good copra are so rare that they must be sold at the normal price and thrown in with the bad. Just as soon as there is a sufficient amount of good-quality copra offered to pay for handling it separately, a new standard will be set and sufficient discrimination shown between good and poor copra to pay the producer for extra care in producing that of good quality.

Three grades of copra are regularly recognized in the Manila market: Cebu Sun Dried, Fair Marketable Manila, and Laguna. A discriminating price of about 75 centavos per picul exists for Sun Dried over Laguna.

The above condition is applicable to the usual local conditions and is not true of the world's market, where a discriminating price is paid for copra dependent on the quality. Inquiries have been received by local merchants asking for terms for the supply of high-grade copra in large quantities. The price quoted was sufficiently higher to warrant the use of greater care and the expenditure of considerable more money in the preparation of the copra. However, under present conditions it is impossible either to buy large quantities of high-grade copra in the local market or to produce the same with existing methods. One shipment of 1,000 tons of high-grade copra from the Philippines would do much toward raising the present standard of our copra in the world's market and to increase the demand for it.

## SUMMARY

The moisture content of representative samples of commercial copra is shown. Tables showing the loss in weight, the rise of temperature, and the presence of notable quantities of carbon dioxide, in the surrounding atmosphere when poorly dried copra

is stored, are included. Well-dried copra does not show this phenomenon of oxidation when stored.

A distinction is made between the true and the apparent loss in oil when copra molds.

A determination of the moisture content necessary for the growth of the four common molds—the white, black, brown, and green—has been made, and the loss in oil resulting from their action on copra for definite periods of time has been found. A description of their habits of growth is included. Data are presented which show that a considerable difference exists in the moisture content of the upper and lower layers of the copra and that the upper layer may contain sufficient moisture for mold growth when the moisture content of the general sample is below the moisture requirement for this growth.

The local copra-drying methods are discussed, and proof is offered of the nonloss of oil when copra is dried in a hot air drier at temperatures ranging from 70° to 100° C.

A method making use of sulphur dioxide has been investigated, and the results are presented.

Methods for the improvement of Philippine copra are suggested, and the difficulties of making changes in the present methods of marketing are considered.

# METHODS FOR THE PRODUCTION OF PURE COCONUT OIL[1]

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The production of copra has always been the most convenient means of handling coconut, since it eliminates the shells and husks from transportation charges and the cost of installation and operation of oil mills. Little attention, particularly in the Philippines, is paid by the producers to the quality of the copra concerned in its relationship to the oil and press cake obtainable. This laboratory has been considering the possibilities of obtaining pure oil direct from the fresh coconuts, thereby eliminating the necessity of turning the nuts into copra with its attendant deterioration, loss of oil, and the refinement of a product which might be originally prepared in a pure condition.

A crude method of obtaining oil from fresh coconuts as practiced in the provinces is as follows. The nuts are husked by breaking on the sharp point of a plowshare, halved with bolos, and the meat is removed and grated in one operation by means of a steel burr driven with pedal attachment. The same operator holds the half nut and drives the burr. The grated meat is transferred to the *caua*, or steaming kettle, where it is mixed with one half its volume of water and steamed for from two to four hours by the application of direct heat from burning shells and husks. The steamed meat is then placed in rattan bags, which are suspended in a perpendicular position between two heavy pieces of wood, and pressure is applied by means of a wooden vice screw. The *gata*, or white emulsion of oil, water, and cellular tissue obtained, is returned to a second caua, where the water is evaporated and the cellular tissue coagulated into a brown mass. This cellular tissue, of high protein content, is used by the Filipinos as a food. The oil is ladeled into earthenware vessels, and the small solid particles remaining are allowed to settle out. No filtering process is resorted to. The oil so obtained is used locally for edible purposes. The press cake is shaken through a bamboo basket in order to disintegrate it and

[1] Received for publication February, 1917.

is then allowed to ferment for a period of three days, with occasional stirring and turning of the meat to hasten fermentation. After the first fermentation period the meat is ground by means of the *iluhan*, a crude apparatus consisting of a heavy roller working back and forth over a flat surface, and is then repressed. The process of fermenting and repressing is carried on daily for from five to seven consecutive days. All of the oil obtained from the various pressings of fermented meat is classed as rancid oil for soap making and similar articles. The *poonac*, or press cake, is used for feeding hogs.

The edible oil represents about one third of the total oil obtained and is of fair quality, having some fatty acids and a slight burnt taste and odor and not being entirely free from color. It commands a somewhat higher price than does the rancid oil. The latter, besides being rancid, is highly colored and contains a high percentage of free fatty acids.

Below are given data showing the amounts of oil remaining in the meat after the various pressings, acid contents of oils, and cost and sale prices of the oil at Pagsanjan in September, 1915. The labor cost for milling the grated coconut meat is not included in the calculation nor is any value assigned to the press cake, although it still contains about 24 per cent oil. These items probably nearly balance under the system used by the Filipinos.

TABLE I.—*Data on the Filipino process for obtaining oil from the fresh coconut.*

| Press cake analysis: | Oil in press cake. | |
|---|---|---|
| After 1st expression (unfermented meat) | per cent | 44.18 |
| After 2d expression (fermented meat) | do. | 36.68 |
| After 4th expression (fermented meat) | do. | 30.68 |
| After 5th expression (fermented meat) | do. | 27.69 |
| After 7th expression (fermented meat) | do. | 23.90 |
| Acidity of oils (oleic): | | |
| Edible oil from evaporated emulsion | do. | 0.6 |
| Rancid oil after 5th expression of rancid meat | do. | 9.5 |
| Cost price of oil from 1,000 nuts: | | |
| Nuts | pesos[a] | 20.00 |
| Husking | do. | .50 |
| Grating | do. | 2.00–2.50 |
| Total | do. | 23.00 |
| Selling price of oil from 1,000 nuts:[a] | | |
| Edible oil 37.85 liters (10 gallons) | do. | 10.50 |
| Rancid oil 75.70 liters (20 gallons) | do. | 20.00 |
| Total | do. | 30.50 |
| Net profit from oil from 1,000 nuts | do. | 7.50 |

[a] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

Mr. O. Vyner, of British North Borneo, reports a recently patented method for obtaining oil from fresh coconuts, which involves the use of modern machinery and which he claims can be extended advantageously to a daily capacity of 10,000 nuts. The following is a brief description of the process as outlined in his letter to the Bureau of Science.

The meat is removed from the shell by means of a small, one man operated machine, with a capacity of 25 nuts per hour. The meat is then carried on an endless chute to roller crushers and then into the grinder where it is rendered into a fine state of division. From the grinder it passes into a large tank called a receiver, where it is thoroughly mixed with a definite quantity of pure water [amount not given]. The mixture is then run into the boiler where it is heated to a certain temperature and the temperature maintained for a period of time [temperature and time control not given]. The boiled material is next allowed to flow over a coarse strainer, the emulsion passing into a container and the pulp transferred to the molder, where the meat is made into cakes for the final pressing. The liquid from the molder also flows into the container. The contents of the container are pumped into the evaporator, where they are heated [temperature not given] until the oil separates from the rest of the liquid, when it is drawn off as the finished product ready for storage. The pulp from the molder is next subjected to high pressure resulting in the elimination of the water from the "poonac" so formed.

We were unable to duplicate these results in laboratory practice, probably due to the fact that a complete description of the process was not given.

We found by repeated trials that freshly grated coconut meat would not give up its oil readily by pressing. When subjected to a pressure of 70 kilograms per square centimeter (1,000 pounds per square inch), over 60 per cent of the total oil remained in the press cake. By treating the meat with water and live steam for a period of three hours before pressing, 80 per cent of the total oil was removed by one pressing. A mechanical agitator used in the above experiment, which beats up and thoroughly stirs the meat and water during the heating, brings more of the oil in contact with the liquid through breaking of the cell walls, so that a greater amount of oil is obtained when the mixture is pressed. The liquid obtained after pressing is a white emulsion, consisting of cellular tissue, oil, and water. Oil prepared from the emulsion by heating over a direct flame as described in the native process is colored and possesses a burnt taste and odor even when small amounts of the emulsion are evaporated. The quality of the oil was not improved by evaporating the water from the emulsion under diminished pressure, since the jellylike mass of cellular tissue and oil remaining must be further heated at a higher temperature completely to coagulate the tissue in

order to free the oil, and this imparts the burnt odor and taste. The centrifugal cream separator suggests itself as a means of removing the water, and while it separates the water very nicely on a small scale, the solid particles of the emulsion rapidly pack into the separating bowl, and the operation must be interrupted while the accumulated fiber is removed. A modified centrifuge might be constructed that would not be subject to this disadvantage.

It was noticed that a large part of the water separated from the emulsion upon standing, and if allowed to stand for a sufficient length of time, microörganisms attack the emulsion, breaking down the tissue with liberation of the oil. The length of time required, together with the high rancidity and acidity of the oil produced, does not commend the process. Attempts were made to liberate the oil from the emulsion by heating with (1) salt, (2) acids, and (3) alkalies, but in all cases the oil was impaired in quality and the separation was not facilitated. Freshly grated coconut meat was heated in an autoclave at from 120–130° C. for as long as four hours, both with and without the addition of water, but did not permit of a greater degree of expression than where live steam was used under ordinary pressure. Similar experiments were made, using an amount of 10 per cent sodium sulphite solution equal to the volume of the meat on the assumption that the coconut meat would be disintegrated as in the making of paper from wood pulp with the sulphite process. This treatment might be used for the manufacture of soap stock oils, as it facilitates the removal of the oil, but the quality of the oil is impaired in both color and taste.

As a result of these preliminary experiments we have determined methods that work successfully in laboratory practice and contain no points which could not be duplicated on a factory scale. The process which was found to yield the best results is outlined as follows:

The meat may be removed from the shells and ground into a fine state of division by either of two methods:

*a.* The process employed in the small oil mills throughout the provinces, which consists in grating out the meat from the half nuts by means of a revolving burr, manipulated with a pedal attachment. One man can grate the meat at the rate of 100 nuts per hour.

*b.* A more modern method for dealing with large quantities of nuts divides the process into two parts. The meat is first freed from the shell by treating the nuts with live steam for a period of from fifteen to thirty minutes. It is convenient to use

a large hopper-shaped box provided with pipes carrying waste steam from the boilers. The treated nuts are opened, and the meat is readily removed with an ordinary copra knife, after which the meat is ground by the machinery employed for grinding copra. The meat prepared by the latter method is in a more finely divided condition than is obtained by the former method. This ground meat is next placed in a cooking vat provided with open pipes for live steam and mechanical beating apparatus, mixed with an equal volume of water, heated, and violently agitated for a period of three hours. By this treatment the oil is washed from the meat, together with some finely divided cellular tissue which forms a white emulsion with the water. After the cooking process the emulsion is strained off and the pulp is passed into a molding machine, where it is pressed into cakes of convenient size for the final pressing by the hydraulic. Press cake so formed would necessarily require drying in order to improve its keeping qualities, since otherwise it would be attacked by microörganisms. The oil remaining could then be removed by further pressing just as in the case of any other copra cake.

The emulsion resulting from the pressing, together with the strained portion, is now run into a storage tank, where it is cooled to a temperature of 15° C. and the temperature maintained for twenty-four hours. The freezing process allows the water to separate from the emulsion, leaving a supernatant layer of solid fat and cellular tissue, at the same time preventing the action of destructive microörganisms. After drawing off the water, the solid layer is allowed to melt by application of gentle heat or simply by standing, until it attains normal Philippine atmosphere temperature. The freezing and melting apparently rupture the cell walls and allow the oil to separate. The separated oil is next run through a filter press which removes all solid materials present, then sterilized at 100° C. for thirty minutes, and stored in air-tight containers. Oil prepared by this method is water white in appearance, possesses a bland coconut odor, and is free from acidity and rancidity. The keeping qualities, even without sterilization, are superior to that from ordinary copra oil. A sample after standing for nine months showed only 0.6 per cent acid (oleic).

A second method for the production of pure coconut oil and a valuable press cake from fresh nuts is outlined below. This does not eliminate drying, but is a continuous process in which the meat is removed from the shells and ground as described under the first method (either *a* or *b*), after which it is dried

and, while still hot, subjected to pressure for the removal of the oil. In the finely divided condition the meat will dry in a current of hot air much more rapidly than when in large pieces, as is practiced in the making of copra. The preparation of shredded coconut, which is carried out by driving air at a temperature of 70°–85° C. over finely divided meat spread on trays, requires only from thirty to sixty minutes for drying to a water content of 5 per cent.[2]

In a small experimental drier devised by us, the meat, after grinding, was dried to 10 per cent moisture content within an hour's time. This percentage of moisture is sufficiently low to prevent the formation of an emulsion. When the meat was expressed in a small horizontal press, over 80 per cent of the total oil was removed in one operation.

TABLE II.—*Data concerning the pressing of freshly grated and partially dried coconut meat. Pressure, 70 kilograms per square centimeter (1,000 pounds per square inch). Temperature, 80 to 85° C.*

| Sample No. | Time. | Loss in weight of original weight. | Water in meat. | Extraction of total oil. | Oil in cake. | Water and cellular tissue in oil. |
|---|---|---|---|---|---|---|
| | *Min.* | *P. ct.* | *P. ct.* | *P. ct.* | *P. ct.* | |
| 1 | 60 | 24.5 | 31.4 | 84 | 31.8 | Much. |
| 2 | 90 | 36 | 9.0 | 87 | 24.7 | None. |
| 3 | 60 | 33.2 | 16.4 | 87 | 29.9 | Some. |
| 4 | 60 | 25 | 33.5 | 70.6 | 44 | Much. |
| 5 | 90 | 39.1 | 25.6 | 76.4 | 27.4 | Little. |
| 7 | 120 | 41 | 12.3 | 86.3 | 22.6 | Practically none. |
| 8 | 120 | 39 | 9.0 | 84.8 | 24.6 | None. |
| 9 | 90 | 30.2 | 5.6 | 89.4 | 22.5 | Do. |

The data on the extraction are valuable for comparative purposes, since they give the efficiency of expression of copra with varying degrees of moisture under identical conditions of expression. A more efficient press would obtain more of the oil, but the ratio of yields with different moisture contents of cake would remain much as they are above. The point of interest is the fact that clear, water-white oil, free from emulsion, can be obtained from cake with a 12 per cent water content.

A type of drier which should be efficient could be constructed along the lines of a sugar drier, or a drier constructed on the plan of that manufactured by the Philadelphia Textile Company would be effective in drying this finely divided meat.

[2] For further data on drying coconut meat, see Walker, *This Journal* (1906), 1, 147.

In this process the meat would be machine-handled from the time it is removed from the shells until the oil and press cake are reached. We estimate that one expeller would be sufficient for a plant handling 45,000 nuts daily, giving an oil output of 6 tons. The market quotation [3] for commercial oil on the Pacific coast at present is 27¼ centavos (13⅝ cents United States currency) per pound, and for Cochin oil the best grade of unrefined coconut oil on the market would be 35 centavos (17.5 cents United States currency) per pound. The oil obtained by the process outlined above is water white and is free from acidity and rancidity; it would command the best market prices. This would mean an increase of 155 pesos per ton over the ordinary commercial oil, the grade to which Philippine oil at present belongs.

Commercial copra press cake finds a place on the market in the form of stock foods and commercial fertilizers. As a stock food it compares favorably with gluten feed, but contains less carbohydrate material and more fat, ash, and fiber. According to data of the Massachusetts Agricultural Experiment Station [4] 100 pounds of coconut meal contains 88.4 therms of net available energy as against 82.7 therms for the gluten feed, due to the higher percentage of fat of the former. (See same bulletin for more data.)

The possibilities of the press cake obtained from the above method are worthy of consideration not only as a stock food, but for human consumption as well. This product is white and clean, containing a small amount of water and pure oil in amounts dependent, of course, upon the efficiency of the pressing.

The keeping qualities would be better than in the case of shredded coconut, because of the lower oil content. Samples stored in closed and open containers for several months underwent no impairment in quality. Nutritive value and description of edible products, which we have prepared from samples of this meal, are as follows:

TABLE III.—*Nutritive value of copra meal from expression of freshly dried coconut meat.*

| | Per cent. |
|---|---|
| Water | 7.35 |
| Oil | 32.14 |
| Ash | 4.05 |
| Crude fiber | 37.12 |
| Protein (N×6.25) | 20.34 |

[3] *Oil, Paint & Drug Reporter* (1916), **90**, 63.
[4] *Bull. Mass. Agr. Exp. Sta.* (1914), 155, 190.

TABLE IV.—*Recipes for the preparation of food products from coconut meal.*

| Product. | Coconut meal. | Flour. | Baking powder. | Sugar. | Eggs. | Milk. | Salt. | Time cooked. | Manner of cooking. |
|---|---|---|---|---|---|---|---|---|---|
| | *Cup.* | *Cup.* | *Teaspoonsful.* | *Cup.* | *Cup.* | *Cup.* | *Teaspoonsful.* | *Mins.* | |
| Coconut oven scones. | ⅓ | ½ | 1 | ¼ | ½ | Sufficient to make batter. | ¼ | 30 | Hot oven. |
| Coconut gems | ½ | ⅔ | 1½ | ⅙ | none | Sufficient to make batter. | ½ | 30 | Do. |
| Coconut griddle cakes. | ½ | ½ | 1 | ------ | 1 | Sufficient to make batter. | ⅓ | until brown | Fried in lard or crisco. |
| Coconut rusks [a] | ⅓ | ½ | 1 | ⅙ | 1 | ¾ | ½ | 30-40 | Hot oven. |
| Coconut bread | ¾ | ¼ | 5 | ¼ | 1 | 1 | ¾ | 30-40 | Do. |

[a] One-half teaspoonful each of nutmeg and cinnamon is added to the dough, and the surface is sprinkled with sugar and cinnamon.

It will be noticed that in all of these products no lard, crisco, or butter is needed for shortening. Water may be substituted in all cases for sweet milk. In view of these laboratory tests it seems possible that coconut meal might be substituted to advantage for wheat flour and lard in the preparation of cheap edible products. It must, however, be borne in mind that the meal used was obtained from pressing freshly dried coconut meat and not from ordinary commercial copra meal; meal from fresh machine-dried copra would be valuable for the same purpose. It seems to us that there is a good opportunity for a plant producing edible oil and press cake for human consumption.

## SUMMARY

Methods used by the Filipinos, together with the results obtained by these methods, are presented.

A method used by Mr. O. Vyner, of British North Borneo, is reported.

Experiments carried out by the Bureau of Science and their results are discussed. The description of a method, devised by us, which makes the grinding, drying, and pressing of coconut meat a continuous process and obviates the many handlings that at present are required, is included.

Recipes for the preparation of food products from clean, pure coconut meat are given.

# THE RANCIDITY OF PHILIPPINE COCONUT OIL [1]

By Harvey C. Brill and Harrison O. Parker

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila*)

The cause, measurement, and prevention of rancidity in oils have engaged the attention of many investigators.

Walker [2] decided that the rancidity of coconut oil arose from the action of heat, light, moisture, and air on the oils. He believes that most of the changes in the oil take place in copra due to the activity of the microörganisms and offers as a possible explanation of the cause of rancidity in pure oils "that a small percentage of fatty acid is oxidized to an oxyacid, which in turn forms a lactone, and (assuming the formation of hydrogen peroxide) the latter would give rise to a peracid, which, in turn, would oxidize the free glycerine to an aldehyde." Walker states that an oil which has been rancid and later refined again becomes rancid more readily than an oil that has never shown rancidity. No explanation for this greater tendency to rancidity is offered by him.

As an estimation of the rancidity of coconut oil he determined the free fatty acids and made the fuchsin-sulphurous acid test for aldehydes and the peroxide test. He disclaims placing any credence on the free fatty acid determination as a measurement of the degree of rancidity of oils and asserts that the ordinary aldehydes are not offensively odorous. Therefore it appears from his results that the rancidity of oils must be due to the presence of compounds other than aldehydes or free fatty acids. Yet he maintains, "The most satisfactory [test for rancidity], in my experience, is that with fuchsin-sulphurous acids, shaking up about equal parts of oil and reagent."

Haller and Lassieur [3] take issue with many other investigators regarding the cause of rancidity when they state that the unpleasant odor of commercial coconut oil is due to the presence of free fatty acids, such as caproic, caprylic, capric, and lauric. In the volatile products from the refining of coconut oil these authors [4] found ketones.

[1] Received for publication March, 1917.

[2] Walker, H. S., *This Journal* (1906), **1**, 1917.

[3] Haller, A., and Lassieur, A., *Compt. rend. Acad. sci.* (1910), **150**, 1013.

[4] Ibid. (1910), **151**, 699.

Lewkowitsch [5] asserts—

> I therefore ascribe the primary cause of rancidity, namely the formation of free fatty acids, to the action of moisture in the presence of soluble ferments, which act as catalysts or accelerators; * * * Rancidity is not due, as is still widely believed, to the presence of free fatty acids alone; in other words, rancidity must not be considered as coterminous with acidity * * * It is only when oxygen and light gain access to the acid fats that the conditions favoring the setting in of rancidity are provided. Rancidity is rather due to the direct oxidation of free fatty acids by the oxygen of the air, assisted and intensified by the exposure to light.

The presence of free fatty acids can be, therefore, considered only the first step in the formation of rancidity.

Butter placed in storage for prolonged periods of time often acquires a rancid odor. This rancidity has been ascribed to the activity of microörganisms by various authorities. The latest of these investigators is Dyer,[6] who has shown by a thorough study of cold-storage butter that the change in flavor is due to the slow oxidation of the nonfatty portions of the butter.

We believe that the nonfatty material in coconut oil has a profound influence on its character, and experiments are now in progress to test this out.

Schmid [7] classifies oils as "sour fats," "rancid fats," and "sour and rancid fats." In coconut oils we have distinct classes of odors existing in the rancid oils, namely, sour odor, possessed especially by some oils made by Filipinos from fresh nuts which are characterized by a high acid value;[8] esterlike [9] and smokelike odors, observed particularly in oils made from moldy copra which has been prepared by the *tapahan* (Filipino grill for drying copra meat) method; and a third with an odor of stale lard, which is shown by sweet coconut oil that has become rancid due to exposure to the air. The investigation now under way will attempt to determine the difference in the chemical character of the various odors and whether the cause of each particular odor is peculiar to it.

The present article deals with the various methods of meas-

[5] Lewkowitsch, J., Chemical Technology and Analysis of Oils, Fats and Waxes. Macmillan & Co., London (1913), **1**, 52.

[6] *Journ. Agr. Research* (1916), **6**, 927.

[7] Schmid, A., *Zeitschr. f. anal. Chem.* (1910), **37**, 301.

[8] For method of preparation see Parker, H. O., and Brill, H. C., *This Journal, Sec. A* (1917), **12**, .

[9] Coconut meat which has been acted upon by bacteria possesses an esterlike odor, and this odor in coconut oil probably arises from the action of the bacteria on the meat before pressing.

uring rancidity which have been recommended by the investigators of rancidity in oils.

One of the methods, which has many advocates, as a test for rancidity is the fuchsin-sulphurous acid color test. Walker [10] reports that in many commercial oils which gave organoleptic tests for rancidity the color test failed to respond, while in many instances oils which were sweet did give color tests. This test, which is known as Schiff's aldehyde test, is considered by some to owe its activity to the presence of active oxygen for results. Aldehydes have the property of activating the oxygen of the air. One of the chemists to investigate the property of aldehydes to give oxygen was Ludwig.[11] He found that the aldehydes investigated by him—acetaldehyde, paraldehyde, propylaldehyde, isobutyraldehyde, and benzaldehyde—lost this power of giving a reaction with potassium iodide if they were previously distilled in a stream of carbon dioxide. Urbain [12] claims that the color, produced by aldehydes with decolorized fuchsin, is the result of a condensation reaction.

Kastle and Loevenhart [13] ascribed the oxidation activity of benzaldehyde to the absorption of oxygen from the air to form benzoyl hydrogen peroxide ($C_6H_5CO$-O-OH). This compound readily gives up one oxygen and forms benzoic acid, which no longer possesses the property of activating the oxygen of the air. These authors believe the activity of oxidizing enzymes arises from a similar reaction.

The fact that certain oils which are unmistakably rancid do not restore the color to decolorized fuchsin, while other oils which are not rancid do produce a color with the reagent, shows that the test is not reliable as an indication of the rancidity of the oil.

Additional objections to the use of the fuchsin-reagent are that it gives a color reaction with compounds other than aldehydes (assuming that aldehydes are present when rancidity exists) and that these colors are difficult and often impossible to distinguish in shade.

An alkaline solution of diazobenzene sulphonic acid reacts with aldehydes in the presence of sodium amalgam to give a violet-red coloration. This reagent was used in the tests recorded in Table I.

Table I gives the color reactions of fuchsin-sulphurous acid

[10] Op. cit.

[11] Ludwig, E., *Ber. d. deutsch. chem. Ges.* (1896), **29**, 1454.

[12] Urbain, G., *Bull. Soc. chim.* (1896), **15**, 455.

[13] Kastle, J. H., and Loevenhart, A. S., *Am. Chem. Journ.* (1901), **26**, 539.

and of diazobenzene sulphonic acid with a few organic acids, alcohols, and aldehydes.

TABLE I.—*Color reactions of organic acids, aldehydes, and alcohols.*

| Name of compound. | Result with fuchsin-sulphurous acid. | Result with diazobenzene sulphonic acid. |
|---|---|---|
| Formic acid | None | Slightly violet. |
| Acetic acid | Faintly violet | Reddish violet. |
| Propionic acid | Violet | Yellow. |
| Butyric acid | do | Cherry red. |
| Valeric acid | do | Yellow. |
| Stearic acid | Faintly violet | Slightly violet after short time. |
| Oleic acid | None | Reddish violet. |
| Glycollic acid | Violet | Deep violet directly. |
| Lactic acid | None | None. |
| Oxalic acid | do | Do. |
| Malonic acid | do | Deep violet after short time. |
| Free fatty acids from coconut oil[a] | Violet | Violet. |
| Formaldehyde | do | Violet (good). |
| Acetaldehyde | do | Do. |
| Paraldehyde | do | Do. |
| Glycerol C. P. (colorless) | None | None. |
| Glycerol (old; slightly colored) | do | Do. |
| Glycerol (old; air passed through for four hours at 30° C.) | do | Do. |
| Methyl alcohol | do | Do. |
| Ethyl alcohol | Violet | Faintly violet. |
| Propyl alchol | None | Do. |
| Butyl alcohol (normal) | Faintly violet | Do. |
| Isobutyl alcohol | Violet | Violet. |
| Butyl alcohol (tertiary) | Faintly violet | Faintly violet. |
| Amyl alcohol (normal) | Violet | Do. |
| Heptyl alcohol (normal) | do | None. |
| Ethylene glycol | do | Red. |
| Acetylacetone | do | Yellow red. |

[a] This coconut oil gave no test with the reagents before saponification.

The compounds used for the color tests were Kahlbaum products. A study of the results indicates that the tests are not due to the presence of aldehydes, since identical reactions occurred with other compounds.[14] Color reactions were given by acetic, propionic, butyric, valeric, stearic, and glycollic acids; by ethyl, butyl (normal), isobutyl, butyl (tertiary), amyl, heptyl, and ethylene alcohols; and by acetyacetone with the fuchsin-sulphurous acid reagent. Positive or confusing tests were given by acetic, butyric, stearic, oleic, glycollic, and malonic acids; by ethyl, butyl (normal), isobutyl (tertiary), amyl (normal),

[14] A more thorough investigation of the property of organic compounds to give color with these reagents is now under way in this laboratory.

and ethylene alcohols; and by acetylacetone with diazobenzene sulphonic acid. Tests were given by the free fatty acids of coconut oil, by formaldehyde, acetaldehyde, and paraldehyde with both reagents, but the four samples of glycerol responded negatively.

Color reactions were given by various alcohols, aldehydes, and acids with diazo-benzene sulphonic acid and with fuchsin-sulphurous acid. As these compounds are Kahlbaum chemically pure products, it hardly seems plausible to assert that the compounds reacting to give the color could be aldehydes present as impurities.

In Table II are recorded some data on coconut oils in the possession of the Bureau of Science.

An examination of the records of Table II reveals some interesting relationships, namely, Nos. 38 and 44, with low acidity, both show rancidity when tested by their organoleptic properties; on the other hand, Nos. 13, 22, 26, 34, 36, 39, 46, and 47 show relatively high acid values compared with that of fresh oil (usually about 0.2 per cent calculated as oleic), but are free from rancid odors. These results indicate that the acidity of coconut oil is not a measurement of the rancidity.

Samples 2, 5, 7, 8, 9, 10, 11, 32, 37, 38, and 45 have a rancid odor, but do not restore the color to decolorized fuchsin, while the color is restored by samples 26, 28, 33, 40, and 41, which do not possess a rancid odor. The existence of no relationship between the restoration of the color of fuchsin and the odor of the oil is indicated by these results. The results with diazobenzene sulphonic acid are equally interesting. Oils with rancid odors which do not give a color are Nos. 1, 3, 8, 9, 10, 38, and 45, and those giving a color but not possessing a rancid odor are Nos. 26, 28, 36, 39, 40, 41, and 42.

If the color with these two reagents arises from the same cause, it is impossible to explain the formation of color products with decolorized fuchsin in the case of samples 1, 3, and 33 and the absence of color of these samples with diazobenzene sulphonic acid, or the color given by Nos. 2, 5, 7, 11, 32, 36, 37, 39, and 42 with diazobenzene sulphonic acid and the absence of color with decolorized fuchsin. Diazobenzene sulphonic acid is considered a more sensitive reagent for the detection of aldehydes than is fuchsin. This explains why color resulted with diazobenzene sulphonic acid, but not with fuchsin, the latter results, but does not explain the preceding results. Oils which agree in all respects in the so-called rancidity tests are Nos. 17, 18, 19, and 27, which possess no rancid odors, no high acidity, and do

TABLE II.—*Properties and reaction of various coconut oils.*[a]

| Sample No. | Description of sample. | Approximate age. | Odor. | Color. | Acidity as oleic acid. | Color with fuchsin-sulphurous acid. | Color with diazobenzene sulphonic acid. |
|---|---|---|---|---|---|---|---|
| | | *Months* | | | *P. ct.* | | |
| 1 | Commercial copra oil | 3 | Esterlike | Practically colorless | 2.1 | Faint violet turning to indigo. | None. |
| 2 | do | 3 | do | Brownish yellow | 1.8 | None | Salmon immediately. |
| 3 | do | 3 | do | Practically colorless | 2.7 | Faint violet | None. |
| 4 | do | 3 | do | do | 2.5 | do | Pink after short standing. |
| 5 | do | 3 | Smokelike | Light yellow | 2.5 | None | Faint violet immediately. |
| 6 | do | 3 | do | do | 2.5 | Faint violet | Do. |
| 7 | do | 3 | do | do | 5.2 | None | Yellowish red immediately. |
| 8 | Pagsanjan oils, edible oil (Sept., 1915) | 18 | Lardlike | Practically colorless | 5.3 | do | None. |
| 9 | do | 18 | do | Light yellow | 2.0 | do | Do. |
| 10 | Pagsanjan oils, Sept., 1915, "Gata" separated oil.[b] | 18 | Sourlike | Practically colorless | 3.0 | do | Do. |
| 11 | Pagsanjan oil, Sept., 1915, "rancid oil" | 18 | do | Brownish yellow | 17.8 | do | Yellowish immediately. |
| 12 | Native-process edible oil (April, 1916) | 12 | Lardlike | Practically colorless | 2.1 | Indigo almost immediately. | Medium violet on standing. |
| 13 | do | 12 | Sweet | do | 1.4 | None | None. |
| 14 | Oil from machine-dried copra | 24 | Lardlike | do | 2.6 | Indigo almost immediately. | Medium violet immediately. |
| 15 | Oil from machine-dried copra (copra 2 years old). | 5 | do | Light yellow | 2.7 | Slightly fainter than 14. | Very faint violet on long standing. |
| 16 | Oil from grated meat, freshly dried, pressed, and filtered; full bottle (Nov., 1916). | 4½ | Sweet | do | 0.2 | None | None. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 17 | Oil from grated meat, freshly dried and pressed; air space (Nov., 1916). | 4½ | do | do | 0.2 | do | Do. |
| 18 | Oil from grated meat, freshly dried, pressed, and filtered; open bottles; sterilized twelve hours at 100° C. (Jan., 1917). | 2 | do | do | 0.2 | do | Do. |
| 19 | Oil by freezing process | 3 | do | do | 0.8 | do | Do. |
| 20 | Oil extracted from good copra | 3 | Lardlike | do | 2.5 | Faint violet | Very faint violet. |
| 21 | Extracted oil from moldy copra (neutralized) | 4½ | Esterlike | do | 1.7 | Indigo almost immediately. | None. |
| 22 | Oil from grated meat freshly dried, pressed, and filtered, open container. | 3½ | Sweet | Practically none | 2.3 | None | Do. |
| 23 | Oil from dealer (prepared by evaporation of emulsion). | 6 | Lardlike | do | 2.2 | Indigo almost immediately. | Faint violet. |
| 24 | Pili nut oil | 6 | do | Brownish yellow | 7.9 | Indigo somewhat fainter than 23. | Dark violet immediately. |
| 25 | Free fatty acids from old coconut oil | | Sourlike | do | 91.5 | Deep violet | Do. |
| 26 | Free fatty acids from fresh, pure coconut oil [c] | 1 | Sweet | Practically none | 125 | Indigo | Faint violet soon. |
| 27 | Oil from grated meat, freshly dried and pressed. Clarified with Fuller's earth and filtered. Sterilized eight hours at 105° C. Oxygen bubbled through thirty-six hours. | 1 | do | do | 0.3 | None | None. |
| 28 | Same process as in No. 27, but not clarified | 1 | do | do | 0.4 | Faint indigo | Very faint violet on long standing. |
| 29 | Filtered oil from fresh meat. Full, stoppered bottle. | 15 | Lardlike | do | 1.5 | do | Do. |
| 30 | Filtered oil from sulphured meat. Full, stoppered bottle. | 15 | do | do | 1.9 | do | Do. |
| 31 | Commercial coconut oil. Rancid oil, native process. | 10 | Sourlike | Brownish yellow | 4.9 | do | Do. |
| 32 | Expeller oil from dealer | 3 | Smokelike | do | 2.8 | None | Salmon immediately. |

[a] These tests were made on April 5, 1917.
[b] For description, see Brill, H. C., et al., *This Journal, Sec. A* (1917), 12, this number.
[c] The original coconut oil gave no color test with either reagent.

TABLE II.—*Properties and reaction of various coconut oils*—Continued.

| Sample No. | Description of sample. | Approximate age. | Odor. | Color. | Acidity as oleic acid. | Color with fuchsin-sulphurous acid. | Color with diazobenzene sulphonic acid. |
|---|---|---|---|---|---|---|---|
| | | *Months* | | | *P. ct.* | | |
| 33 | Filtered oil from fresh meat. Full, stoppered bottle. | 3 | Sweet | Practically none | 0.2 | Very faint indigo | None. |
| 34 | Pili nut oil from fresh nuts; filtered | 1 | do | Light yellow | 2.2 | None | Do. |
| 35 | Commercial coconut oil | 2 | Smokelike | do | 5.1 | Very faint indigo | Faint violet soon. |
| 36 | Pure Lugga olive oil, for culinary purposes | | Sweet | Brownish yellow | 2.2 | None | Very faint violet on long standing. |
| 37 | Pure Lugga olive oil from Bureau of Science storeroom. | | Lardlike | Greenish yellow | 2.2 | do | Do. |
| 38 | Cotton seed oil from Bureau of Science storeroom. | | do | Practically none | 0.3 | do | None. |
| 39 | Castor oil from Bureau of Science storeroom | | Sweet | do | 1.5 | do | Very faint violet on long standing. |
| 40 | Unfiltered oil from grated meat, freshly dried and pressed (Feb. 15, 1917). | 1½ | do | do | 0.4 | Faint indigo | Faint violet soon. |
| 41 | Filtered oil from grated meat, freshly dried and pressed (Jan. 20, 1917). | 2 | do | do | 0.6 | do | Do. |
| 42 | Oil from grated meat, freshly dried and pressed, filtered three times through Fuller's earth, not sterilized; in open container. | 3 | do | do | 0.4 | None | Faint violet. |
| 43 | Oil from machine-dried copra (copra one and one-half years old). | 24 | Lardlike | do | 4.5 | Indigo almost immediately. | Deep violet immediately. |
| 44 | Oil from grated meat, freshly dried and pressed (air space over oil). | 4 | do | do | 0.4 | Violet immediately | Violet immediately. |
| 45 | Oil 32, neutralized with NaOH, washed and filtered. | 3 | Smokelike | Light yellow | | None | None. |
| 46 | Oil 11, steam-distilled one hour just before test. | 18 | Sweet | do | 17.4 | do | Do. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 47 | Oil 11, steam-distilled three hours just before test. | 18 | ......do | ......do | 17.6 | ......do | Do. |
| 48 | Oil 34, treated with sodium hydrogen sulphate, washed and filtered just before test. | 3 | Smokelike | ......do | 3.0 | Deep violet immediately. | Deep violet immediately. |

not give any color with either reagent, and Nos. 4, 12, 20, 21, 23, 24, 25, 29, 30, 31, 35, 43, 44, and 48, which show color with both reagents and possess a high acidity and rancid odor. In a total of forty-eight oils with four tests for rancidity being used, one or more of these tests do not agree with the others in thirty cases.

The organoleptic properties are the most dependable tests for rancidity. In Table III the relationships of the other three tests to the organoleptic properties are given.

TABLE III.—*Relationships of rancidity test to the organoleptic properties.*

| Test. | Disagreements. | Agreements. |
|---|---|---|
| | *Per cent.* | *Per cent.* |
| Acidity | 21 | 79 |
| Diazobenzene sulphonic acid | 29 | 71 |
| Decolorized fuchsin | 33 | 67 |

From Table III it appears that high acidity is a more reliable indication of the rancidity of an oil than the reactions with diazobenzene sulphonic acid or decolorized fuchsin, but this does not prove that rancidity is coterminous with acidity. They occur simultaneously in many cases, but the one is not a necessary corollary of the other. When oils of high acidity are steam-distilled, the residue no longer possesses a rancid odor, but has lost very little in total acidity. Samples 46 and 47 bring this out very prominently. The acidity in these samples remains high, but the rancidity, judged by the odor, has been lost. Sample 45, which had been neutralized with sodium hydroxide and carefully washed, was not freed of its odor though freed of its acidity. Sample 48, which was washed with a solution of sodium hydrogen sulphite to rid it of any aldehydes that might be present, still retained its rancid odor. If rancid odor is due to the presence of aldehydes, this sample should have lost its odor.

Issoglio [15] describes a confirmatory test for rancidity in olive oils, which he calls the "oxidisability value." He states that when the oxidisability value exceeds 15 it will be usually found that the oil is rancid or has undergone some other change.

Table IV contains some oxidisability values and some acetyl values, together with other data on Philippine coconut oils before and after distillation with live steam.

[15] Issoglio, G., *Ann. chim. applic.* (1916), 6, 1.

TABLE IV.—*Oxidisability, acetyl and iodine values of various oils.*

| Sample No.[a] | Rancid or sweet.[b] | Kind of oil. | Oxidizability value. | Acetyl value. | Iodine value. | Acidity of original oil as oleic acid. | Residual oil from steam treatment. | | | Distillate from steam treatment. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Acidity as oleic acid. | Color with decolorized fuchsin. | Color with diazobenzene sulphonic acid. | Acidity as oleic acid. | Color with decolorized fuchsin. | Color with diazobenzene sulphonic acid. |
| | | | | | | *P. ct.* | *P. ct.* | | | *P. ct.* | | |
| 4 | + | Coconut | 21.0 | 10.5 | 8.9 | 2.5 | 2.3 | None | Faint violet | 0.2 | None | None. |
| 11 | + | do | 15.8 | 21.7 | 7.6 | 17.8 | 18.0 | do | Yellow | 0.5 | do | Do. |
| 14 | + | do | 47.0 | 10.8 | 5.0 | 2.6 | 2.6 | Indigo | Faint violet | 0.3 | Faint violet | Faint violet. |
| 15 | + | do | 10.0 | 9.6 | 5.9 | 2.7 | 2.8 | do | Violet | 0.1 | do | Very faint violet. |
| 19 | — | do | 3.0 | 15.6 | 7.5 | 0.8 | 0.9 | Faint violet | Faint violet | none. | None | None. |
| 24 | + | Pili nut | 26.0 | 30.2 | | 17.9 | 18.0 | Greenish blue | Violet | 0.2 | Violet | Faint violet. |
| 29 | + | Coconut | 0.9 | 12.5 | 6.6 | 1.5 | 1.4 | Indigo | do | none. | None | None. |
| 30 | + | do | 1.5 | 17.3 | 8.1 | 1.9 | 1.8 | do | Faint violet | 0.1 | do | Do. |
| 31 | + | do | 9.3 | 7.0 | 7.2 | 4.9 | 4.8 | Faint indigo | Very faint violet | 0.2 | do | Very faint violet. |
| 32 | + | do | 41.0 | 9.5 | 8.4 | 2.8 | 2.8 | None | Violet | 0.1 | do | Do. |
| 33 | — | do | 0.8 | 8.0 | 5.5 | 0.2 | 0.2 | Faint indigo | Faint violet | none. | do | None. |
| 34 | — | Pili nut | 7.6 | 15.6 | | 2.2 | 1.9 | None | Very faint violet | none. | do | Do. |
| 35 | + | Coconut | 38.0 | 9.8 | 8.5 | 5.1 | 5.0 | do | Faint violet | 0.1 | do | Very faint violet. |
| 36 | — | Olive | 0.7 | 12.3 | | 2.2 | 2.0 | Greenish blue | do | none. | do | None. |
| 37 | + | do | 2.9 | 11.6 | | 2.2 | 2.2 | do | Violet | do | do | Do. |
| 38 | + | Cotton seed | 4.6 | 42.0 | | 0.3 | 0.2 | do | Very faint | do | do | Do. |
| 39 | — | Castor | 4.4 | 140.1 | | 1.5 | 1.4 | do | Violet | do | do | Do. |
| 44 | + | Coconut | 40.0 | 12.7 | 6.0 | 0.4 | 0.3 | Indigo | do | do | do | Faint violet. |

[a] Sample numbers correspond to sample numbers of Table II.

[b] + means rancid; — means sweet.

The oxidizability value for the coconut oils exceeded 15 (the maximum value given by sweet olive oils according to Issoglio) in samples 4, 11, 14, 32, 35, and 44. All of these samples were rancid, but samples 15, 30, 31, and 37, which were rancid, gave values lower than 15. It is possible that a limiting value of 15 for coconut oil may be too high, but the limit cannot be brought low enough to include all the rancid oils examined by us and still exclude the sweet oils. The test appears to be a good confirmatory one, since no sweet oils gave high results.

The acetyl values of several oils were determined in an endeavor to ascertain if any relationship exists between them and the rancidity. The lowest value, 7.0, was given by No. 31, a rancid oil, while the highest value, 21.7, was shown by No. 11, also a rancid oil. The value of the acetyl number is dependent on the presence of the hydroxyl group. Lewkowitsch makes no mention of the presence of hydroxy acids in coconut oil. The only unsaturated acid generally accepted as present in coconut oil is oleic, which exists in comparatively small quantities. It is possible that when rancidity takes place one of the reactions occurring is the formation of oxy or dioxy stearic acid from oleic acid, but this would not account for an acetyl number of a magnitude of 21.7 for coconut oil. The residue of the increase must arise from the freeing of the hydroxyl groups of the glyceryl radical. A high acetyl number should be, therefore, associated with a high acid value in the case of coconut oil. A study of the contents of Table IV proves that this relationship does not exist in all instances. It is possible that where the hydrolysis of the oil takes place in the copra itself much or all of the free glycerol remains in the press cake or is further decomposed, resulting in a low acetyl number along with a high acid number.

The iodine number of an oil with a high acetyl number should be correspondingly low if the increased value of the acetyl number arises from the oxidation of the unsaturated acids. The data in Table IV do not prove the validity of this assumption, since no definite relationship appears to exist between the values of these two chemical constants.

Further tests were made on four oils. These data are recorded in Table V.

TABLE V.—*Comparative constants of four coconut oils.*

| Sample No. | Iodine number (Hanus value). | | Acetyl value. | | Reichert Meissl No. | | Free fatty acid as oleic. | | Soluble fatty acid as butyric. | | Color with decolorized fuchsin. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | Residue from soluble fatty acid determination. | | | |
| | | | | | | | | | | | O | T | O | | T | |
| | O[b] | T[b] | O | T | O | T | O | T | O | T | | | Oil. | Aqueous solution. | Oil. | Aqueous solution. |
| 11 | 7.6 | 7.0 | 21.7 | 25.6 | 8.3 | 8.0 | 17.8 | 16.6 | 1.1 | 0.8 | None | None | None | None | None | None. |
| 19 | 7.5 | 6.4 | 5.6 | 4.7 | 8.1 | 7.8 | 0.8 | 0.6 | 0.6 | 1.7 | Slight indigo | Very slight indigo. | Slight violet | do | Slight violet | Do. |
| 32 | 8.4 | 7.1 | 9.5 | 9.4 | 8.0 | 7.3 | 2.8 | 2.6 | 1.4 | 0.8 | None | None | None | do | None | Do. |
| [a]50 | 6.0 | 4.5 | 12.7 | 10.7 | 9.0 | 8.5 | 2.0 | 1.2 | 1.5 | 2.2 | Indigo | Indigo | do | do | do | Do. |

[a] Oil made by Bureau of Science from fresh, clean copra. Originally sweet and pure. Now possesses lardlike odor.

[b] "O" means original oil; "T" means oil after subjection to steam distillation.

Sample II was sour in odor, No. 19 was a sweet oil, No. 32 was smokelike in odor, while No. 50 was lardlike in odor.

The iodine values of the steam-treated oils are lower in all four cases than are the iodine values of the original oils. Apparently the unsaturated compounds are either volatile in the steam or they are partially changed to saturated compounds by the live steam.

The acetyl values in three cases are lower for the treated oils. The hydroxy compounds appear to be somewhat soluble in the live steam. The higher value in the case of No. 11 probably arises from the hydrolysis of the glyceryl esters of the fatty acids by the live steam. The free fatty acids which are present in comparatively large quantities in this sample act as accelerators of this hydrolysis of the neutral oil, or the mono- and diglycerides may be further hydrolized to free fatty acid and glycerol and to the monoglyceride and glycerol, respectively. The Reichert Meissl number shows the variation one would expect with the steam treatment of the oils. No difference in its value was found for the sweet and the rancid oils.

The free fatty acids and their relationship to the rancidity have been already discussed. This constant is included here in order that the acid value for No. 50 might be tabulated.

The relative values of the soluble fatty acids vary for the original and treated oils in a manner difficult to explain. Further data will be necessary before any conclusions can be drawn from this constant in regard to the effect of steam distillation. Dakin [16] has shown that when oleic acid is oxidized with hydrogen peroxide azelaic acid is formed and all fatty acids from formic up to and including stearic are oxidized by mild oxidizing agents. If the formation of rancidity is caused or accompanied by an oxidation, one of the first changes to take place would be the breaking down of the unsaturated acids into simpler acids with an accompanying increase in the value of the soluble fatty acids. Consequently the value of the soluble fatty acids of rancid oils should be greater than the value for the sweet oils. This generalization holds true for the original oils that have been tabulated in Table V.

The milk from the coconut contains both oxidase- and peroxidaselike enzymes. These enzymes are not found in the pure, fresh coconut meat, and their presence in such meat is probably due to contamination from the milk of the meat. However,

[16] Dakin, H. D., *Journ. Biol. Chem.* (1908), 4, 63 and 237.

copra which has been attacked by molds or copra with milk adhering to it has oxidasing enzymes present, and when such copra is ground and pressed, some of this enzyme may be separated with the oil. If such enzymes were present, they would in all probability have an important influence on the formation of rancidity.

The oils described in this article were examined for oxidizing enzymes. No. 5 gave a faint test, No. 15 gave a fair test, and No. 28 gave a strong test for peroxidaselike enzymes with tincture of gum guaiacum and hydrogen peroxide. All the rest responded negatively for oxidizing enzymes with these reagents. No conclusion can be drawn concerning the cause for the presence of the enzymes in these samples and their absence in all the others. No. 5 is a commercial sample of oil with a smokelike odor, which indicates that it was made from tapahan-dried copra. In method of preparation and history it is very similar to Nos. 1, 2, 3, 4, 5, and 7. No. 15 is an oil made from a machine-dried copra. This sample is very similar to No. 14 in history. No. 28, made from fresh copra, is pure and sweet and similar in most respects to No. 27. The enzyme here must arise from contamination from the milk of the nut. The activity of the other two must arise from the molds that grew on the copra before it was milled, the milling temperature not being high enough to destroy their activity.

Why only these three gave positive tests is difficult of explanation. The color appeared in them only after the sample had stood in contact with the reagent for a short time.

Tests were made on the fresh coconut meat for lipase, but we were unable to confirm the positive results reported by other investigators.[17] Walker[18] reports no lipase or zymogen present in the fresh meat, and our results are in accord with his. Where the meat of the coconut is subjected to a comparatively high temperature during the process of drying, the activity of any enzyme doubtless would be greatly decreased if not totally destroyed. But the hydrolysis of oils in the presence of moisture undoubtedly takes place to an appreciable extent at relatively low temperatures. In the experiments recorded by Deming, where comparatively large amounts of mineral acids were used "to activate the zymogen," we believe the acid alone is sufficient to bring about the hydrolysis recorded by this observ-

[17] De Kruff, *Bull. Dept. Agr. Indes Néerl.* (1906), 4, 8. Deming, H. G., *Phil. Agr. For.* (1914), 3, 33.

[18] Walker, H. S., *This Journal, Sec. A* (1908), 3, 111.

er. Acetic acid failed to give like results when used by us, and were a zymogen present this acid should activate it.

## CONCLUSIONS

The color tests with decolorized fuchsin and with diazobenzene sulphonic acid are not reliable tests for rancidity. High acidity of oils is not coterminous with rancidity. Steam distillation removes rancidity, but makes very slight changes in the acidity; neutralization with alkali and washing removes the acidity but not the rancidity. The Reichert Meissl number in the few cases studied indicated no close relationship between this constant and the rancidity. No conclusions could be drawn from the magnitude of the iodine value. The soluble fatty acids show a relationship which indicates that this constant might be of value in an estimation of the rancidity of an oil. The acetyl value may be of value in indicating rancidity, but is not a measure of the degree of rancidity. The oxidizability number appears to be a good confirmatory test for rancidity, but a few samples of oils undoubtedly rancid gave low oxidizability values. However, where the value was high, the oil was always rancid.

Further work on the acetyl value, the oxidizability value, the soluble fatty acids, and the test for the presence of oxidizing enzymes and their action should yield valuable data.

Control samples have been stored for the study of these constants.

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## Section A

## CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES



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VOL. XII MAY, 1917 No. 3

## DESTRUCTIVE DISTILLATION OF PHILIPPINE WOODS[1]

By A. H. WELLS

*(From the Laboratory of Organic Chemistry, Bureau of Science, Manila)*

In the United States and other countries the destructive distillation of waste wood has become a large and growing industry.

In order to furnish some idea as to the possible introduction of such an industry into the Philippine Islands, certain classes of woods were selected and the relative yields of products were determined on representative specimens.

TABLE I.—*Classification of commercial woods used for destructive distillation.*

| Botanical name. | Commercial name. | Group.[a] | Hardness.[a] | Specific gravity.[b] | Moisture.[b] |
|---|---|---|---|---|---|
| | | | | | *P. cent.* |
| *Rhizophora* sp | Bacauan | 4 | Very hard | 0.925 | 8.1 |
| *Bruguiera parviflora* W. & A. | Langarai | 4 | do | 1.053 | 9.0 |
| *Avicennia officinalis* L | Api-api | 4 | do | 0.754 | 7.7 |
| *Intsia bijuga* (Colebr.) O. Ktze | Ipil | 1 | Hard | 0.933 | 6.7 |
| *Hopea* sp | Yacal | 1 | do | 0.930 | 7.2 |
| *Shorea guiso* (Blanco) Blume | Guijo | 2 | do | 0.716 | 7.4 |
| *Dipterocarpus* sp | Apitong | 3 | Medium hard | 0.721 | 10.0 |
| *Shorea polysperma* (Blanco) Merr | Tanguili | 3 | do | 0.492 | 7.8 |
| *Pterocarpus* sp | Narra | 1 | do | 0.630 | 6.3 |
| *Pentacme contorta* (Vid.) M. & R. | White lauan | 4 | Soft | 0.458 | 8.6 |
| *Anisoptera thurifera* Blanco | Palosapis | 3 | do | 0.711 | 8.4 |
| *Pinus insularis* Endl | Benguet pine | 4 | do | 0.687 | 9.2 |

[a] Group and hardness are taken from *Annual Reps. P. I. Bur. For.* (1906–1914).
[b] Specific gravity and moisture determination were made on the specimens used.

The percentage of charcoal made in the Philippines from wood other than that cut for such specific purpose is very small. There exists in the Philippines a vast amount of wood of a waste nature, the possible utilization of which might be a great benefit to certain industries. Throughout the Islands in the timber

[1] Received for publication January 30, 1917.

regions the annual production of waste wood about certain mills has so increased that the question of its disposal is now a problem before the mill men. Another possible source of waste wood is that from the cutch, or tan bark, industry. During the fiscal year 1914 there were taken from the public forests of the Philippine Islands 2,793,295 kilograms of tan bark.[2] The highest percentage of this bark comes from the mangrove swamps. These swamps cover extensive areas in Mindanao, Palawan, and other islands in the southern parts of the Archipelago. If means for a profitable utilization of the wood from these trees could be devised, it seems probable that a stimulus would be given to a larger tan bark industry.

The woods selected for distillation are representative of the timber trees that are found in greatest abundance and also of the trees furnishing tan barks.

Bacauan, langarai, and api-api represent classes of woods which comprise the greater portion of the forest areas in the swampy regions of Mindanao. The bark stripped from trees of the bacauan family is especially of value as a source of tannins, while the wood itself is little used as lumber and offers a ready supply for distillation. The area of these mangrove swamps is approximately 207,200 hectares.[3] Apitong, tangili, guijo, yacal, white lauan, and palosapis belong to the Dipterocarpaceæ and are representative of some of the principal timber trees that are milled in the Philippines. The dipterocarp forests are estimated by the Bureau of Forestry as covering 70 per cent of the total area of the commercial forests of the Islands. Ipil and narra belong to the Leguminosæ and are representative of that class of timber trees. Benguet pine, *Pinus insularis* Endl., is the common pine, found principally in the Benguet region. It is milled particularly in northern parts of Luzon, where it extends over an approximate area of 518,000 hectares.

The specimens of wood used for furnishing the analytical data were taken from several sources.

The bacauan, the api-api, and the langarai were identified and cut in Mindanao swamps and were shipped to the Bureau of Science, where they were allowed to season for five years. The pine logs were obtained from the Benguet region through the courtesy of the Bureau of Forestry. The other specimens were identified and purchased from reliable lumber dealers in Manila, care being taken in selecting samples that seemed to

[2] *Rept. P. I. Bur. For. for 1914* (1915) and ibid. *for 1915* (1916).
[3] Cox, Alvin J., *This Journal, Sec. A* (1911), 7, 2.

show a likeness in size, color, specific gravity, and apparent moisture content.

A separate lot of each kind of woods was kiln-dried until the moisture content seemed uniform. The whole specimen was then placed in a tight container, and from this the daily charge was taken and distilled. From eight to thirteen charges were made from each specimen and specific gravity and moisture determination made on each charge. The averages for these determinations are found in Table I. The specific gravities were taken by the usual method. The measure of the moisture was not that of the total volatile substance below 108° C., which in many cases would contain oils, but a measure of the volatile part taken up by pure calcium oxide. The determination was made by passing the volatile matter through a tube of calcium oxide, afterward heating the tube for three hours at a temperature of 185° C. sufficiently high to volatilize all oils present and yet not to drive off water from the partially slaked lime.

Destructive distillation was selected as the method for distilling the woods, the reason being that it seemed to give the highest yields of the commercial products—methyl alcohol, acetic acid, tars, and charcoal. Steam distillation might have shown interesting results regarding the resinous products obtainable, and this method may be applied later to certain classes of woods that are known to be high in resinous content. The destructive method is that in general use in the distillation of hard-wood waste, and for that reason also it is used here to furnish experimental data of comparative value.

In determining a laboratory method for the distillation, it seemed advisable to have a temperature control. During 1913 experiments were made in this laboratory by utilizing an oil-jacketed retort. In the use of the oil-jacketed retort a heavy hydrocarbon oil was heated and kept in circulation by the aid of an electrically controlled Kinney pump, which was connected to the retort so that it supplied cold oil from the storage tank and also accelerated the circulation of the hot oil about the retort. Coils of various sizes and forms were tried as heating surfaces for the oil. The most satisfactory surface seemed to be that of a piece of iron pipe 17 centimeters long by 13.5 centimeters in diameter, capped at both ends, the caps being bored to accommodate a 1-inch circulation pipe.

The heat was furnished by two Meker burners connected to the laboratory gas supply. The loss of heat by radiation was cut down by placing a heavy shell of asbestos cement over the

retort. But this method gave neither the close temperature control nor other results desired. Also the cylinder oils submitted for the bath gave unsatisfactory results under high temperatures; consequently the method was abandoned.

In June, 1916, an improved experimental plant was set up and operated. The plant consisted of a cylindrical iron retort mounted at a suitable height and heated electrically in such a manner that the inside temperature could be closely controlled over a range in temperature of 500° C. The capacity of the retort was from 10 to 15 kilograms, varying with the specific gravity of the wood. The four heating coils were made of No. 18 "ni-chrome" wire arranged to give an approximate reading of 10 amperes for each coil. The wires were wound about the retort connected in parallels, insulated from the sides of the retort by a layer of asbestos board, and covered on the outside by a shell filled with a layer of asbestos powder 6 centimeters thick. This outer layer left slight chance for loss of heat.

The control of the temperature was effected by inserting resistance and by breaking the main circuit. Each coil in the resistance cut from the circuit gave a rise of 2 amperes current. This arrangement gave a very satisfactory temperature control.

The condensation of the distillates and the scrubbing of the noncondensible gases occurred in a coil made of lead pipe 2.5 centimeters (1 inch) in diameter fitted inside an ordinary barrel of strong material and connected on the outside to a small tower from which extended pieces of glass tubing 400 centimeters long and of diminishing diameter. This tubing aided in condensing the lighter product and carried off the noncondensible gases. The tar trap for catching the heavy distillates was placed between the retort and the condenser. It consisted of a piece of iron pipe 10 centimeters (4 inches) in diameter, capped at both ends and fitted with a pet-cock at the bottom. Standardized thermometers were used in noting the temperature changes, which were taken at the center of the charge. Corrections for the emergent stem of the thermometer were made in accordance with the common formula $0.00016\ (T-t)\ N$.

In order to get comparative data, both fast and slow runs were made on the lots of woods. In operating the still, the weighed charge was placed into the retort and the current was applied. The fast or uncontrolled runs were made with 35 to 40 amperes of a 110 volt direct current and occupied about nine hours before practical completion. No effort was made to control the heat except at the beginning of the exothermal reac-

tion, which began between 265° and 275° C. During this period the current was shut off until the reaction subsided in violence and was then immediately applied. The current was shut off to prevent a loss by overtaxing the condensing system.

In the slow, or controlled, distillation the current was so applied that the apparent moisture was first driven off. The moisture was considered driven off when a temperature was reached at which there was a decided pause in the distillation. This pause occurred at different temperatures for different classes of wood and varied between the temperatures 121° and 180° C. at the center of the retort. Later the passage of more current was allowed so as to afford the minimum temperature for distillation. At the beginning of the exothermic distillation the main circuit was broken, and no current was allowed through until the rise in temperature ceased and distillation lessened. The rise in temperature during this period seldom exceeded 20° C. After passing this period of exothermic reaction, the distillation dropped off rapidly and the application of current was gradually increased up to a temperature of about 330° C. and was increased rapidly to 550° C. In collecting the distillate, graduated cylinders were used.

Samples of pyroligneous distillate from each distillation were analyzed for percentages of wood alcohol and acetic acid. Such analyses taken on fast runs were compared with analyses of products from controlled runs, and the results were tabulated in averages.

TABLE II.—*Showing the average percentages of wood alcohol and acetic acid obtained from a fast and from a slow distillation.*

| Wood. | Slow distillation. | | Fast distillation. | |
|---|---|---|---|---|
| | Methyl alcohol. | Acetic acid. | Methyl alcohol. | Acetic acid. |
| Apitong | 0.91 | 3.80 | 0.72 | 3.91 |
| Tanguili | 1.23 | 2.92 | 1.10 | 2.85 |
| Lauan | 1.20 | 2.90 | 1.11 | 2.63 |
| Guijo | 1.55 | 4.70 | 1.31 | 5.18 |
| Yacal | 0.93 | 4.61 | 0.92 | 4.25 |
| Palosapis | 0.74 | 3.83 | 0.62 | 3.62 |
| Ipil | 1.61 | 4.40 | 1.41 | 4.42 |
| Narra | 1.36 | 4.37 | 1.24 | 4.77 |
| Benguet pine | 0.82 | 2.12 | 0.80 | 2.51 |
| Bacauan | 2.12 | 5.16 | 1.56 | 4.84 |
| Api-api | 1.71 | 4.66 | 1.42 | 4.27 |
| Langarai | 1.84 | 4.95 | 1.17 | 4.50 |
| Coconut shell | 1.01 | 6.31 | 1.00 | 6.16 |

The percentages in Table II are calculated on the moisture-free sample and not on the sample as kiln-dried wood. The figures expressing wood alcohol also include slight percentages of acetone present. Klar's[4] method was used in the chemical analyses, together with those used by the United States Bureau of Chemistry[5] and the Philippine Bureau of Science.

The results expressed in Table II show that a distillation proceeding under controlled temperature condition gives in most cases an increase in yields of methyl alcohol; that is, the average percentage of alcohol obtained by slow distillation is in all cases higher than that obtained by fast distillation. The mangrove woods bacauan, api-api, and langarai gave the highest yields in alcohol and acetic acid. Of the twelve woods distilled, those highest in resinous content gave the lowest percentages of these two products. The figures obtained for the yields of acetic acid do not show a relationship constant enough to warrant the statement that the controlled distillation gives higher percentages of acetic acid, although the greater number of distillations high in acetic acid are those carried out under the controlled distillation.

In most cases the distillate began passing over at 110° to 117° C. and continued at approximately the same rate up to 265° to 275° C., when the exothermic action of the decomposition tended to accelerate the flow. The clear liquor passing off below 180° considered as moisture gave no qualitative tests for the presence of alcohol, but did show an acid reaction toward litmus.

Distillation under temperature control on certain hardwoods in the United States shows interesting results.[6] Lowering the temperature of the reaction and decreasing the speed of the distillation in the laboratory at the period of exothermal reaction increased the yield of methyl alcohol 45 per cent. The application of this method to a commercial retort indicated possible yields of alcohol 30 per cent higher than by the usual methods of firing and an increase of 15 per cent in yields of acetate of lime. The best results were obtained by first rapidly removing the moisture content of the charge and later decreasing the heat at a period just before the destructive distillation began. This method of temperature control gave promise of being entirely applicable in the commercial plant.

[4] Klar, M. Technologie der Holzverkolung. Julius Springer, Berlin (1910).

[5] *Circ. U. S. Dept. Agr., Bur. Chem.* (1907), No. 63.

[6] Palmer, R. C., *Journ. Ind. & Eng. Chem.* (1915), 7, 668.

The yields from the destructive distillation of various Philippine woods have been tabulated and placed below. All of the calculations are expressed as percentage yields based on the moisture-free wood. The pyroligneous distillate represents the acid liquor free from tars. The percentage gas is taken by difference.

TABLE III.—*Percentage yields of various products from Philippine woods.*

| Wood. | Pyroligneous distillate. | Settled tars. | Distilled tars. | Floating tars. | Noncondensible gases. | Charcoal. | Methyl alcohol. | Acid as 100 per cent acetic acid. | Number of runs. |
|---|---|---|---|---|---|---|---|---|---|
| Apitong | 39.7 | 6.2 | 5.6 | 8 | 15.1 | 32.6 | .91 | 3.80 | 13 |
| Tanguile | 39.8 | 4.8 | 2.7 | -------- | 18.8 | 33.9 | 1.23 | 2.92 | 8 |
| Lauan | 36.6 | 3.6 | 3.2 | -------- | 23.4 | 33.2 | 1.20 | 2.90 | 8 |
| Guijo | 35.5 | 3.9 | 2.3 | -------- | 20.0 | 38.3 | 1.55 | 4.70 | 8 |
| Yacal | 34.6 | 3.4 | 2.1 | 1.1 | 20.3 | 38.5 | .93 | 4.61 | 8 |
| Palosapis | 39.9 | 2.6 | 1.2 | -------- | 19.7 | 36.6 | .74 | 3.83 | 8 |
| Ipil | 32.4 | 3.9 | 2.0 | .9 | 19.1 | 41.7 | 1.61 | 4.40 | 8 |
| Narra | 39.4 | 5.7 | 2.1 | -------- | 16.0 | 36.8 | 1.36 | 4.37 | 8 |
| Benguet pine | 38.9 | 5.5 | 3.6 | 1.2 | 15.1 | 35.7 | .82 | 2.12 | 8 |
| Bacauan | 39.5 | 2.7 | 1.4 | -------- | 21.2 | 35.2 | 2.12 | 5.16 | 8 |
| Langarai | 40.8 | 2.9 | 1.3 | -------- | 22.9 | 32.1 | 1.84 | 4.95 | 8 |
| Api-api | 43.4 | 3.4 | 1.8 | -------- | 19.0 | 32.4 | 1.71 | 4.66 | 8 |
| Coconut shell | 41.3 | 6.9 | 3.2 | -------- | 16.2 | 32.5 | 1.0 | 6.31 | 5 |

The pyroligneous distillate as it comes from the retort ranges in color from pale straw, given by palosapis, to a deep brownish red, given by narra. Titrations were made on ten fractions covering the periods of complete runs. The fraction showing the highest percentages of acid varied with the class of wood distilled, but fell between the temperatures 285° and 325° C. Table III gives the yields expressed as 100 per cent acetic acid on dry weight of wood based on a slow or controlled distillation. Bacauan, langarai, and api-api give the highest percentage yields of methyl alcohol and acetic acid. The woods giving the lowest yields are woods known as soft woods and woods containing resin.

Results obtained in the United States showed[7] yields of acetic acid for maple, beech, and birch (three hardwoods) as high as 6.30, 6.28, and 6.96 per cent, respectively, the percentages being based on per-unit weight of the oven-dried wood distilled. It may be that distillation of other classes of Philippine hardwoods will show higher percentage yields than those obtained from the woods already examined.

[7] Palmer, loc. cit.

Determinations of acetone in the pyroligneous distillate were neglected except for qualitative tests showing its presence. Many of the distillates, especially those from the resinous woods, contained aldehyde and higher ketonic bodies and substances influencing the reduction of the iodide. For the determination of the alcohol the method suggested by Stritar and Zeidler [8] was used, but was afterward replaced by the modified methyl iodide method. With the hardwoods free from light oil the percentage could be taken from the specific gravity of the distillate according to the methods of Klar.[9]

### TARS

The tars were classified as settled tars, dissolved or "boiled" tars, and floating tars.

The settled tar was the portion taken from the tar trap added to that which settled at the bottom of the pyroligneous liquor. Dissolved tars are those lighter portions dissolved in the pyroligneous liquor, but separated by boiling off. The floating tars were very light products found floating on the surface of the distillate and in the scrubbing tower. They gave tests for methyl alcohol, acetone methylated compounds, ketones, terpenes, and neutral hydrocarbon oils. The total tar included all three of the classes, and as such it was used as an analytical sample in the case of each wood distilled.

The composition of oils originating from the destructive distillation of wood has been thoroughly studied by Fraps.[10] Working on tar from hardwood, he arrived at the following results, which show the complex nature of a hardwood tar:

(1) The wood oil examined is a mixture of a homologous series of different classes of compounds.

(2) It probably contains the series of aldehydes $C_nH_{2n}O$, corresponding to the series of saturated acids $C_nH_{2n}O_2$, found in wood vinegar, which goes up to and includes caproic acid. The quantity of aldehydes is so small that only one could be positively identified, valeric aldehyde. Acetic aldehyde and propionic aldehyde have been found in wood oil by other investigators, and these facts justify the first statement. It contains furfural in minute quantity.

(3) It contains the series of ketones $C_nH_{2n}O$, of which dimethylketone, methylethylketone, methylpropylketone, and probably methyl-*n*-butylketone and diethylketone have been detected.

(4) It contains the ring ketone, cyclopentanone, and other ring ketones.

[8] *Zeitschr. f. anal. Chem.* (1904), **43**, 381.

[9] Loc. cit.

[10] Fraps, G. S., *Am. Chem. Journ.* (1901), **25**, 26.

(5) It contains no mesityl oxide nor methylcyclopentanone.

(6) It contains nitriles in minute quantity.

(7) It contains the methyl esters of the saturated acids, $C_nH_{2n}O_2$, found in wood vinegar, including methyl acetate, methyl propionate, methyl *n*-butyrate, methyl *n*-valerate, very probably methyl caproate, and methyl heptoate and possibly methyl isobutyrate. The acid corresponding to methyl heptoate has not yet been found in wood vinegar. The percentage of ethereal salts decreases as their boiling-points rise, the lower-boiling ones being present in considerable quantity, the higher ones in very small quantity. One might conclude from this that the quantity of the corresponding acids in wood vinegar decrease with increase in boiling-point.

(8) It contains the esters of unsaturated acids.

(9) It contains methylfurane, and furanes which can be hydrolyzed by cold, strong hydrochloric acid to diketones. The furanes include dimethylfurane, trimethylfurane, and higher furanes.

(10) It contains no dimethylacetal, nor appreciable quantities of pyridines or alcohols.

(11) It contains compounds which take up hydrochloric acid and bromine, and are therefore unsaturated.

(12) It contains the aromatic hydrocarbons, toluene and xylene, and probably cumene and cymene.

(13) It contains creosote.

(14) It contains phenol ethers in minute quantity.

(15) The higher boiling oils, freed from ketones, aldehydes, ethereal salts, and creosote can be separated into two parts by glacial acetic acid, the one soluble in that substance, the other insoluble. Both absorb bromine readily.

Samples of tars from the Philippine woods were fractionated in a high distilling flask without the use of the Hempel column, and the results obtained are tabulated in average.

TABLE IV.—*Showing average percentage of light and heavy oils passing over in fractionation of the various tars.*

[Numbers give percentages.]

| Name. | Wood oil below 100° C. | Light oils, 100°-150° C. | Heavy oils, 150°-250° C. | Distillate above 250° C. |
|---|---|---|---|---|
| Bacauan | 0.5 | 6.0 | 19 | 15 |
| Langarai | 0.8 | 6.2 | 20 | 15 |
| Api-api | 0.3 | 0.6 | 20 | 16 |
| Ipil | 2.5 | 2.3 | 32 | 0 |
| Yakal | 3.0 | 6.0 | 35 | 0 |
| Guijo | 2.0 | 5.0 | 40 | 0 |
| Apitong | 2.2 | 2.2 | 28.0 | 0 |
| Tanguili | 1.8 | 2.6 | 21 | 14 |
| Narra | 2.4 | 2.5 | 54.0 | 0 |
| White lauan | 2.0 | 1.5 | 20 | 0 |
| Palosapis | 2.2 | 2.5 | 20 | 18 |
| Benguet pine | 2.8 | 6.0 | 29 | 11 |
| Coconut shell | 2.5 | 8.0 | 50 | 0 |

The samples taken for fractionation were freed from water by settling and by repeated use of separatory funnels. Yet on fractionation a high percentage of water was found dissolved in certain of the tars. In the cases of palosapis, white lauan, pine, and guijo the percentage of water ranged from 20 to 34, while in the others it seldom was above 10 per cent and was even as low as 2.6, as in api-api.

The fractions passing over below 100° C. have a specific gravity of 0.958–0.998; are colorless, quickly turning yellow to brown; are very inflammable; and have a strong, characteristic odor. They gave reactions for aldehydes and ketones by the acid sulphite method. Attempts to form terpene compounds from the fractions from the resinous woods gave slight results. A few crystals of terpene hydrate were obtained.

The fraction passing over between 150° and 250° C. and containing the creosote fraction ranged from pale yellow to brown. All specimens quickly darkened. The specific gravity varies from 1.010 to 1.028. The green and the blue oils began passing over at 230° C., accompanied by a small amount of water, indicating decomposition of some of the compounds present. This decomposition and liberation of water was greater with the tars from the apitong and other resinous woods than from the bacauan and less resinous ones. The green anthracene oil preceded the blue coming over in distillation. The fractions from each of the tars showed marked reaction with caustic soda and gave rapid reaction for esters. Two cubic centimeters of the oil added to 100 cubic centimeters of a 20 per cent solution of sodium hydroxide set to a heavy, flocculent white precipitate. About 70 per cent of this compound decomposes upon washing free of alkali or treatment with solvents. The percentages of oil unacted upon by the sodium hydroxide seemed very low. No further work was done on this portion of the tars. It is proposed at a later date to fractionate larger quantities of this fraction, getting the exact creosote fraction and the percentage of phenolic compounds present. The fractions passing over above 250° C. are semisolid and usually red. They contain the highest fractions of the wood tar, together with certain high boiling fractions of the wood resins and their decomposition compounds. The residue after fractionation is a vitreous black pitch, having a conchoidal fracture and rather high melting point. It is slightly soluble in alcohol, chloroform, and ether and is moderately soluble in carbon disulphide, acetone, benzol, and xylene.

The charcoal taken from the retort is steel gray to black. It has a metallic luster and a conchoidal fracture. The charcoal from all the specimens, excepting tanguili, lauan, pine, and palo-sapis, is heavy and has a decided metallic ring when dropped upon a hard surface. The yields are from 32.1 to 41.7 per cent, calculated on the moisture-free sample. All of the specimens are hard to ignite and burn without flame, smoke, or odor of tarry matter. This class of charcoal would fill all the requirements of a charcoal for domestic purposes, while some of the woods would furnish an excellent charcoal for the iron industry in the Philippines.

Table V shows the results of an analysis of bacauan charcoal that came from a charge heated to 550° C. The sample was taken from an old lot of bacauan charcoal that had stood in the laboratory for a year.

TABLE V.—*Analysis of bacauan charcoal.*

| CHARCOAL. | Per cent. |
|---|---|
| Moisture (110° C.) | 5.71 |
| Volatile combustible matter | 23.79 |
| Fixed carbon | 67.21 |
| Ash | 3.29 |
| Total | 100.00 |
| Available calories | 6799 |
| Gross calories | 7242 |

| ASH.[a] | Per cent. |
|---|---|
| Silica ($SiO_2$) | 2.98 |
| Iron and aluminum oxides ($R_2O_3$) | 2.95 |
| Calcium oxide ($CaO$) | 61.81 |
| Magnesium oxide ($MgO$) | 2.72 |
| Potassium oxide ($K_2O$) | 2.43 |
| Sodium oxide ($Na_2O$) | 8.93 |
| Phosphoric anhydride ($P_2O_5$) | 1.21 |
| Sulphuric anhydride ($SO_3$) | 2.29 |
| Chlorine ($Cl$) | 0.12 |
| Carbon dioxide (undetermined) | 14.56 |
| | 100.00 |

[a] Analyzed by A. S. Argüelles.

The volatile combustible matter seems somewhat high. The calorific values are excellent and probably higher than any value that could be obtained on charcoals made by the Filipino process of burning. The analysis of the ash indicates that bacauan charcoal might be unsuitable for the manufacture of

pig iron for use in the foundries in the Philippines, due to the high percentage of sulphur which it contains.

Cox [11] has shown that there are many woods in the Islands from which the charcoal obtained is entirely free from sulphur and is suitable for use in the smelter. Certain features shown in the analysis of the ash, such as the high percentages of calcium and sodium oxides, may be possibly explained by the fact that the mangroves are distinctly salt-water species occurring in tidelands. The high calorific value places bacauan charcoal as a high-grade fuel for all domestic purposes, and for such purposes there is a great demand for charcoal in the Philippines.

Coconut-shell charcoal possesses remarkable absorptive properties. Such charcoal was used by Wright and Smith [12] for filling the absorption tubes used in their quantitative determinations of radium emanation.

The matter of first cost and operation expenditures is one of individual calculation, depending upon certain local conditions.[13]

The production costs, costs of installation, and production values received in the United States in the distillation of hardwoods have been discussed in some detail.[14]

French [15] finds the production cost to be approximately 17.70 pesos and the production value of crude products 19.82 pesos, giving a profit of 2.12 pesos per cord. He places the cost of installation, eliminating the cost of wood supply, at 4,000 pesos per cord per day production. These figures are for a plant producing crude products from hardwoods.

In determining whether a plant may prove profitable or not, many factors must be taken into consideration.

Through the courtesy of a manufacturer of wood-distillation plants [16] this Bureau has been furnished with a few of the leading questions that should be considered as important factors in plans for a wood-distillation industry.

1. How much wood, and of what quality, is to be worked per year, and in how many working days? What is the price of sufficiently split wood at the place where the factory is situated?

[11] Cox, A. J., Philippine firewood, *This Journal, Sec. A* (1911), **6**, 10.

[12] Wright, J. R., and Smith, O. F., *This Journal, Sec. A* (1914), **9**, 54.

[13] Klar, loc. cit.

[14] French, E. H., *Journ. Ind. & Eng. Chem.* (1915), **7**, 55.

[15] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

[16] Mr. F. H. Meyer, Hannover-Hainholz.

2. What is the weight per cubic meter, or what is the form of the wood used? How long does it lie before it is put in work?

3. What products are principally intended to be manufactured:

| | |
|---|---|
| Charcoal. | Anhydrous tar. |
| Charcoal bricks. | Tar oils and creosote. |
| Brown acetate of lime. | Crude wood spirit of turpentine. |
| Gray acetate of lime. | White deodoriferous pine oil. |
| Crude wood spirit. | Pine tar oil. |
| Refined wood spirit. | Crystallized acetate of sodium. |
| Pure methyl-columbia spirit. | Acetate of sodium, free of water. |
| Acetic acid in all kinds of quality. | Formaldehyde. |
| Acetic acid for vinegar. | Paraformaldehyde. |
| Acetone. | |

4. Is there a market for charcoal, and at what price?

5. Is there a market for tar, and at what price?

6. What kind of fuel may be had and at what price?

7. Is cooling water to be had (state whether fresh or salt water), and what is the mean temperature?

8. Is running water in the neighborhood?

9. Describe the local conditions (distance to nearest railroad station or steamship landing place, harbor, etc., as well as character and condition of roads, etc.).

10. Is there any junction for railway or ship?

11. What is the freight for the products as far as the next place of consumption?

12. What is the freight for apparatus and machinery from manufacturer to place of factory?

13. Are there any buildings to be utilized?

14. Are there any repair shops and how large are they?

15. Are there gratuitous plots of land existing?

16. What are the prices for building materials, such as brick, wood, mortar, etc.?

17. What is the price for finished buildings above the ground: in brick, in framework, in sheet-iron roofs?

18. What is the price for high-furnace-masonry, of brick stone, or chamotte?

19. What is the price for iron-fittings for furnaces per hundred pounds?

It may be readily seen that many of these questions might be answered favorably to the installation of a plant in the Philippines, while at the present time others make it seem impossible as a commercial success.

From a study of the statistics of the Islands it seems probable that a market for the products of a wood-distillation industry could be found in the Philippines and near-by ports. Wood alcohol is used commercially as a denaturant and as a solvent for fats, oils, and resins. It is also used in the manufacture of aniline colors, smokeless powder, and formaldehyde and in

various other chemical industries. Acetic acid is used in the manufacture of compounds used in the dye and paint industries. Acetone is also made from the acetates formed in the process. Acetone is used commercially as a solvent for resins and other compounds; it is also used in the nitro cellulose industry and in the preparation of many pharmaceutical compounds. The tars obtained by destructive distillation can be treated and certain fractions used in turpentine substitutes, cheap varnishes, lubricating oils and greases, inks, leather, soap and cement industries, and for impregnating timbers and ropes.

The crude tars from the Philippine dipterocarps, being high in percentages of resins and oils, should prove very satisfactory as an impregnating or coating substance for ropes and calking used in ship building. Also, as many are high in creosote fraction, their use as a disinfectant or spray for sanitary purposes would furnish a reasonably cheap and efficient substitute for the more expensive mixtures now employed throughout the Islands. The pitch can be used for coating purposes.

Certain conditions are essential for the successful operation of a distillation plant. The first essential is a supply of the raw material of the proper quality and in large quantities that are easily accessible. This not being obtainable, the plant should be one accommodated only to the needs of the mill for clearing away the accumulation of waste wood and sawdust, which may hinder proper operation of the mill. However, in this case it must be observed that the use of small retorts of a capacity of 0.25 to 1 cord would require a disproportionately greater expenditure for wages, for fuel, and for repairs than would the larger retort systems. Likewise the percentage yields are greatly reduced, due to the overheating in the small retort.

A plant erected for supplying products to the Philippine market would probably manufacture charcoal, gray acetate, refined wood spirit, tar oils, and creosote. All of these products have a market and could be used in Philippine arts and trades with the possible exception of the gray acetate, for which use might be made by its conversion into acetic acid or acetone.

## CONCLUSIONS

Specimens from twelve kinds of wood have been submitted to destructive distillation.

A furnace, heated electrically, has been devised to furnish controlled as well as noncontrolled distillations.

The yields of methyl alcohol, acetic acid (100 per cent), charcoal, and tars have been tabulated to show average percentages of products obtained by laboratory practice.

Controlled distillation has shown results higher than those of the noncontrolled distillation in average percentage yields of methyl alcohol and acetic acid. These results are analogous to those found by Palmer.[17]

A short discussion of costs and operating expenses is added.

[17] Loc. cit.

# THE POSSIBLE MAXIMUM VITAMINE CONTENT OF SOME PHILIPPINE VEGETABLES [1]

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Recent investigations have proved that a diet composed of the proper proportions of fat, protein, and carbohydrates is not necessarily an adequate diet for the maintenance of health and growth. Other ingredients must be present; for example, inorganic salts must be present in sufficient quantities.[2]

The absence of certain either-soluble [3] substances is prejudicial to health. This substance has been named "fat soluble A" by McCollum,[4] because of its presence in certain natural fats.

Besides the above-required constituents, another substance, known under the various names "vitamine," [5] "oryzanin," [6] and "water-soluble B," [7] is necessary.

No reliable quantitative methods for the determination of this vitamine constituent have been perfected. In the processes used for its isolation, much of it is undoubtedly broken up into simpler substances,[8] or the antineuritic principle may be due to the presence of a number of bodies. The latter assumption is considerably strengthened by the results obtained by the use of various substances [9] in the treatment of beriberi. A further

[1] Received for publication April, 1917.

[2] Osborne, T. B., and Mendel, L. B., Feeding experiments with isolated food-substances, *Publ. Carnegie Inst. Washington* (1911), No. 156, Parts I and II; and *Science* (1911), 34, 722. McCollum, E. V., and Davis, M., *Journ. Biol. Chem.* (1913), 14, 40. Hart, E. B., and McCollum, E. V., ibid. (1914), 19, 373.

[3] McCollum, E. V., and Davis, M., ibid. (1913), 15, 167. Osborne, T. B., and Mendel, L. B., ibid. (1913), 15, 332.

[4] McCollum, E. V., Simmonds, N., and Pitz, W., ibid. (1916), 28, 153.

[5] Funk, C., *Journ. Physiol.* (1912), 43, 395.

[6] Suzuki, U., Shimamura, T., and Odake, S., *Biochem. Zeitschr.* (1912), 43, 89.

[7] McCollum, E. V., and Kennedy, C., *Journ. Biol. Chem.* (1916), 24, 491.

[8] For a brief bibliography of methods, see Williams, R. R., *This Journal, Sec. A* (1916), 11, 49.

[9] Williams, loc. cit. and *Journ. Biol. Chem.* (1916), 25, 437. Williams, R. R., and Saleeby, N. M., *This Journal, Sec. B* (1915), 10, 99. Williams, R. R., and Seidell, Atherton, *Journ. Biol. Chem.* (1916), 26, 431.

confirmation of the probability of the existence of a number of antineuritic substances in rice polishings, yeast, wheat, and bran, which are antineuritic in character, is the recent discovery by Williams [10] of the peculiar action toward polyneuritic pigeons of the hydroxypyridines, when they undergo dynamic isomerism, and of the similar action of the vitamines isolated from autolyzed yeast.[11]

If the vitamine content of foods does consist of a number of distinct chemical compounds, the difficulty of quantitatively determining it is readily seen. However, some attempts have been made to make such an estimate. Phosphotungstic acid in alkaline solution gives a blue color reaction with the antineuritic substances.[12] Phosphomolybdic acid gives a similar color reaction.[13] The intensity of the color is dependent on the concentration of the vitamine. The handicaps attached to these methods are that no standard exists that can be used for comparison and that other compounds give similar color reactions.

The quantitative isolation is unsuccessful because of the presence of nitrogen compounds, which either accompany the vitamine or are the result of its decomposition. Vedder and Williams [14] report that three successive extractions of rice polishing with alcohol did not extract all the antineuritic properties of the polishings.

Funk [15] has made an attempt to determine the vitamine content of milk in the following manner: The milk was distilled in a partial vacuum at 30° C. It was then powdered and dried to constant weight. The powder was shaken with alcohol for two hours and filtered, and the filtrate was evaporated to dryness. The residue was extracted with water, acidified with sulphuric acid, and treated with phosphotungstic acid. The nitrogen of the phosphotungstic acid precipitate was determined by the Kjeldahl method. By this method Funk estimates the vitamine content of milk to range from 1 to 3 centigrams per liter or from 0.001 to 0.003 per cent.

[10] Williams, loc. cit.

[11] Williams and Seidell, loc. cit.

[12] Drummond, J. C., and Funk, C., *Biochem. Journ.* (1914), **8**, 598. Folin, O., and Macallum, A. B., *Journ. Biol. Chem.* (1912), **11**, 265; (1912), **13**, 363.

[13] Folin, O., and Denis, W., ibid. (1912), **12**, 239. Funk, C., and Macallum, A. B., *Biochem. Journ.* (1913), **7**, 365.

[14] Vedder, E. B., and Williams, R. R., *This Journal, Sec. B* (1913), **8**, 175.

[15] Funk, C., *Biochem Journ.* (1913), **7**, 211.

In a subsequent communication Drummond and Funk [16] report that all the nitrogen of vitamine is not obtained by means of the Kjeldahl method; so the results recorded above for milk are probably low. Compounds containing the pyridine ring possess this same property of resisting digestion with sulphuric acid for the determination of nitrogen.[17] Approximately three fourths of the nitrogen of such bodies were obtained by this method.

A method based upon this property of pyridine derivatives has been employed by the authors for the determination of the possible vitamine content of some vegetables grown in the Philippine Islands.

### DETERMINATION OF THE VITAMINE CONTENT OF VEGETABLES

A portion of the fresh vegetable was dried at a low temperature and very finely ground, and 100 grams of the ground foodstuff was exhaustively extracted with methyl alcohol. The alcohol was evaporated at low temperature, and the residue was taken up in water and filtered. The filtrate was acidified with sufficient sulphuric acid to make a concentration of 5 per cent. Phosphotungstic acid was added to this solution to precipitate the antineuritic substance. After standing for from four to eight hours, the precipitate was filtered off, washed with 5 per cent sulphuric acid and finally with alcohol, and dried in a desiccator over sulphuric acid. The nitrogen was determined in this residue by both the Kjeldahl and Dumas methods.

Weighings of the precipitates and nitrogen determinations were made to serve as checks. These determinations are included in Table I. The calculations were made on the vegetables [18] as they were prepared for the table.

The values for the vitamine content of Philippine vegetables found by this method are usually higher than the results found by Funk [19] for milk. However, they are presented here because they have comparative value and for the purpose of stimulating further investigation in quantitative determination of these constituents.

[16] Drummond, J. C., and Funk, C., *Biochem. Journ.* (1914), 8, 598.

[17] Brill, H. C., and Agcaoili, F., *This Journal, Sec. A* (1917), 12, Kjeldahl process.

[18] For description of Philippine vegetables, see Agcaoili, Francisco, ibid., *Sec. A* (1916), 11, 91.

[19] Funk, C., loc. cit.

TABLE I.—*The possible maximum content of some Philippine vegetables.*

| Sample. | Nitrogen in original sample by Kjeldahl. | Alcohol extract. | Nitrogen in alcohol extract by Kjeldahl. | Original nitrogen extracted by alcohol. | Phosphotungstic acid precipitate based on 100 grams of samples. | Nitrogen in phosphotungstic acid precipitate by— | | Original nitrogen in phosphotungstic acid precipitate calculated from Kjeldahl results. | Vitamine in original samples calculated from nitrogen by—[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Kjeldahl. | Dumas. | | Kjeldahl. | Dumas. | Difference.[b] |
| | *P. cent.* | *P. cent.* | *P. cent.* | *P. cent.* | *grams.* | *P. cent.* | *P. cent.* | *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| Camote | 0.172 | 1.52 | 0.33 | 2.92 | 0.10 | 1.239 | 1.408 | .72 | 0.0024 | 0.0028 | 0.0016 |
| Sincamas | 0.084 | 2.16 | 0.61 | 15.69 | 1.26 | 0.907 | 0.873 | 13.62 | 0.0228 | 0.0220 | 0.0220 |
| Radish | 0.097 | 1.41 | 1.419 | 20.71 | 0.44 | 1.260 | ------- | 5.78 | 0.0144 | ------- | ------- |
| Squash | 0.066 | 1.23 | 0.93 | 17.33 | 0.35 | 0.922 | 1.168 | 4.89 | 0.0064 | 0.0084 | 0.0080 |
| Eggplant | 0.229 | 1.75 | 2.10 | 16.05 | 1.32 | 1.587 | 1.770 | 9.15 | 0.0420 | 0.0448 | 0.0112 |
| Gourd | 0.050 | 0.83 | 0.78 | 12.95 | 0.14 | 1.102 | 0.878 | 3.09 | 0.0030 | 0.0024 | 0.0024 |
| Lima beans, dry | 2.574 | 3.67 | 1.33 | 1.91 | 1.15 | 1.400 | 1.876 | 0.63 | 0.0322 | 0.0430 | 0.0432 |
| Spinach | 0.319 | 0.71 | 3.71 | 8.26 | 0.32 | 2.566 | 2.892 | 2.58 | 0.0164 | 0.0184 | 0.0080 |
| Pasao | 0.440 | 1.39 | 1.446 | 4.59 | 0.89 | 0.699 | ------- | 1.41 | 0.0162 | ------- | ------- |
| Batao | 0.439 | 0.32 | ------- | ------- | 0.22 | 0.856 | 1.500 | 0.43 | 0.0040 | 0.0066 | 0.0066 |
| Onion | 0.273 | 2.93 | 1.08 | 11.57 | 0.90 | 2.030 | ------- | 6.66 | 0.0364 | ------- | ------- |
| Cowpeas, fresh | 0.393 | 0.38 | ------- | ------- | 0.28 | 1.203 | 1.282 | 0.86 | 0.0068 | 0.0072 | 0.0016 |
| String beans, fresh | 0.518 | 0.40 | ------- | ------- | 0.60 | 1.209 | 1.210 | 1.40 | 0.0144 | 0.0146 | 0.0008 |
| Mongo, dry | 3.630 | 1.91 | 1.53 | 0.81 | 1.17 | ------- | 1.430 | ------- | ------- | 0.0326 | ------- |
| White beans | 3.500 | 2.15 | ------- | ------- | 1.56 | 0.792 | 1.883 | 0.36 | 0.0246 | 0.0588 | [c]0.0246 |
| Soy beans, green, dry | 5.650 | 8.65 | 1.082 | 1.66 | 1.18 | 1.215 | 1.893 | 0.25 | 0.0288 | 0.0446 | [c]0.0288 |
| Soy beans, yellow, dry | 5.224 | 8.00 | 0.869 | 1.33 | 1.42 | 1.273 | 2.677 | 0.35 | 0.0362 | 0.0760 | [c]0.0362 |
| Rice, highly polished | 1.463 | 0.10 | ------- | ------- | 0.05 | 1.764 | ------- | 0.06 | 0.0024 | ------- | ------- |
| Tiqui-tiqui | 1.841 | 1.34 | 1.616 | 1.18 | 0.25 | 1.930 | 2.979 | 0.26 | 0.0098 | 0.0148 | [c]0.0098 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bay malt | 1.424 | 3.42 | 1.192 | 2.86 | 1.13 | 1.275 | 1.515 | 1.01 | 0.0288 | 0.0344 | 0.0224 |
| Banana | 0.211 | 10.95 | 0.345 | 17.91 | 4.12 | 0.313 | 0.396 | 5.96 | 0.0256 | 0.0324 | 0.0256 |

[a] The percentage of nitrogen in the antineuritic substances in beer yeast is approximately 50. [See Williams, R. R., and Seidell, A., *Journ. Biol. Chem.* (1916), **26**, 431.] The yield would be approximately five times the results recorded here if they were calculated according to Funk. [See Funk, C., *Journ. Physiol.* (1913), **46**, 177; and Drummond, J. C., and Funk, C., *Biochem. Journ.* (1914), **8**, 598.

[b] This value is obtained by finding the difference between the values for the Kjeldahl and Dumas methods and multiplying this difference by four. Approximately one fourth of the nitrogen is not obtained by the Kjeldahl method from pyridine and its derivatives.

[c] The value here would have been greater than the value found by the Dumas method, which would be manifestly impossible; therefore the latter value is adopted.

SUMMARY

Methods for the quantitative estimation of the vitamine content of foods are discussed.

A method based on the different values for nitrogen in pyridine ring bodies obtained by the use of the Kjeldahl and the Dumas methods is presented. A table with some results for Philippine vegetables is given.

# THE EFFECT OF CALCIUM SULPHATE ON CEMENT [1]

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Calcium sulphate in the form of either gypsum or plaster of Paris is almost universally used to control the setting of cement. The practice has led to extensive research in the attempt to determine the reaction between the two substances and the amount of calcium sulphate that can be added without causing harmful effects. As a result of these investigations some points are fairly well established. A number of writers [2] agree that the retardation of set caused by the addition of calcium sulphate is proportional to the amount added, only within certain limits; that is, the setting time cannot be increased without limit by adding more and more of this substance. On the contrary, after a certain point is reached, further additions cause an acceleration of the set.

Many believe that the permissible amount of calcium sulphate added to a cement should depend to some extent on the conditions to which the concrete made from it is to be exposed. Several countries, among which are France,[3] Japan,[4] and Argentina,[5] specify that a cement, intended for construction exposed to sea water, shall have a lower sulphuric anhydride ($SO_3$) content than one to be used under ordinary conditions.

The German Portland Cement Manufacturers' Association [6] recommended that "a uniform permissible maximum limit of $SO_3$, namely 2.5 per cent, be generally adopted in Specifications for Portland Cement, whatever may be the purpose for which

[1] Received for publication November 13, 1916.

[2] Carpenter, R. C., *Eng. Digest* (1908), **3**, 385. Rohland, P., *Stahl u. Eisen* (1908), **28**, 1815. Reibling, W. C., and Reyes, F. D., *This Journal, Sec. A* (1911), **6**, 225.

[3] *Ciment* (1912), **17**, 213.

[4] *Mitt. Zentralstell. Ford. Deut. Port. Zem. Ind.* (1912), **1**, 167.

[5] Ibid. (1912), **1**, 305.

[6] Report of the International Association for testing materials (1912), Sec. 2, article $XVII_4$, 1. (Translated by G. Salter.)

the cement is intended." This recommendation was made on the basis of results obtained with only two cements:

The materials used consisted of a Portland cement (S), containing 1.19% of $SO_3$ and employed for all purposes, marine structures included, and another Portland cement (B), which contained only a very small proportion of $SO_3$, namely 0.57%.

In both cases the raising of the $SO_3$-content to 2.5% by the addition of gypsum, increased the tensile strength, both in fresh and sea water.

In the summary of the paper it stated that—

From these results it follows indubitably that the presence of up to 2.5% of $SO_3$ in Portland cement, produces no injurious effects of any kind, whether in sea water or fresh water.

No matter how conclusive these results appear, or how carefully the work was carried on, it is impossible to settle such an important question by the behavior of only two cements, particularly in the face of contradictory evidence obtained by other investigators.

It is generally conceded that an excessive amount of sulphuric anhydride in a cement is harmful. All specifications mention an upper limit, though not all agree what this limit shall be.[7] Meade [8] says:

Although the presence of calcium sulphate in small quantities is beneficial to cement, there is no doubt that a quantity exceeding 4 or 5 per cent is injurious.

According to Kühl,[9] the sulphuric anhydride content of a cement should not exceed 2 per cent. Rigby [10] states:

In making some experiments with cement by adding plaster of Paris by mixing the two materials in different proportions, I found that if I exceeded 4½ per cent of the latter the briquettes subsequently made from the mixture either broke up after being placed in water for a time, or, if they retained their shape, they were very much cracked and gave a very poor test.

Bates [11] found that while higher sulphuric anhydride content

[7] Though the specifications of various nations for the upper limit of sulphuric anhydride are often taken as directly comparable, this is not the case. For instance, in the British specifications, 2.75 per cent sulphuric anhydride does not refer to the sulphur present as sulphate only, but means the total sulphur calculated to $SO_3$. (See British Standard Specifications for Portland Cement. Revised, March, 1915.)

[8] Meade, R. K., Portland Cement. Chemical Publishing Co., Easton, Pa. (1906), 31.

[9] Kühl, H., *Mitt. Zentralstell. Ford. Deut. Port. Zem. Ind.* (1913), 2, 108.

[10] Rigby, J. S., *Journ. Soc. Chem. Ind.* (1890), 9, 254.

[11] Bates, P. H., *Proc. Am. Soc. Test. Materials* (1915), 15, II, 126.

(up to 2.5 per cent) in some cases increased the strength of neat briquettes, it caused considerable expansion. In attempting to compare some of the papers on the subject, considerable confusion arises from the terminology of various writers. Some of them refer to the percentage of gypsum added to cement and others to the percentage of plaster of Paris; as a rule, they do not state the percentage of sulphuric anhydride. Others mention simply calcium sulphate, and the reader has no means of knowing in which form it was added. Although the effects of the two substances are similar,[12] there is a considerable difference in the amount of sulphuric anhydride in the commercial products. Different cements require varying amounts of calcium sulphate for the purpose of controlling the set. However, there must be some limit specified for the addition of material subsequent to calcination to avoid adulteration by unscrupulous manufacturers. The specifications state the maximum amount that can be allowed with safety. It remains to investigate the region between this amount and that definitely known to be injurious. It seems likely that the specifications of the countries that make allowance for the conditions to which concrete is to be exposed show an advance in the right direction and that in addition to this there should be some relation between the composition of the cement and the sulphuric anhydride allowed. Until the subject is better known, safety demands that upper limits should be kept well below the amounts known to be harmful.

The present work was undertaken to determine the effect of various amounts of calcium sulphate on several cements on the local market and to study in some detail the behavior of a cement made from raw materials available to the Bureau of Science for investigation. The finished cements investigated are from five different factories and are herein designated as *A*, *B*, *C*, *D*, and *E*. Each contained a certain amount of calcium sulphate placed there by the manufacturer. Various amounts of plaster of Paris were added to each, giving increasing amounts of sulphuric anhydride up to about 10 per cent. Investigation of the other cement, designated by *F*, started with the clinker, which contained only a trace of sulphuric anhydride. The setting time on each sample was determined as a preliminary test. These were used as a guide to determine the percentages of sulphuric anhydride best suited to extended tests. Tables I and

[12] Meade, op. cit., 307.

II show the analyses and the physical tests made on the cements as received.

TABLE I.—*Chemical analyses of cements as received.*[a]

[Numbers give percentages.]

| | Cement— | | | | | |
|---|---|---|---|---|---|---|
| | A. | B. | C. | D. | E. | F. |
| Loss on ignition | 2.50 | 2.80 | 1.50 | 2.40 | 2.00 | |
| Insoluble residue | 0.30 | 0.60 | 0.30 | 0.80 | 0.45 | |
| Silica ($SiO_2$) | 21.10 | 20.00 | 22.50 | 18.80 | 18.95 | 22.32 |
| Alumina ($Al_2O_3$) | 8.76 | 8.86 | 7.58 | 9.18 | 9.52 | 8.21 |
| Ferric oxide ($Fe_2O_3$) | 1.42 | 1.34 | 1.12 | 1.12 | 1.38 | 3.64 |
| Calcium oxide (CaO) | 63.10 | 63.00 | 63.00 | 64.10 | 63.80 | 63.15 |
| Magnesia (MgO) | 1.26 | 1.34 | 1.74 | 1.12 | 1.80 | 1.62 |
| Sulphuric anhydride ($SO_3$) | 0.67 | 0.86 | 1.34 | 1.34 | 1.24 | trace |
| Potassium and sodium oxides ($K_2O$, $Na_2O$) | 0.93 | 1.16 | 0.87 | 1.16 | 0.87 | 1.09 |

[a] Most of these analyses were made by Francisco Peña, inorganic chemist, Bureau of Science.

TABLE II.—*Physical tests of cements as received.*

| Brand.[a] | Fineness. | | Specific gravity. | Initial set. | Final set. |
|---|---|---|---|---|---|
| | Passing 200-mesh sieve. | Passing 100-mesh sieve. | | | |
| | *Per cent.* | *Per cent.* | | *H. m.* | *H. m.* |
| A | 87.6 | 99.0 | 3.12 | 5 15 | 9 6 |
| B | 81.6 | 99.0 | 3.10 | 3 55 | 6 40 |
| C | 89.6 | 99.0 | 3.16 | 4 32 | 7 16 |
| D | 85.6 | 98.6 | 3.10 | 4 26 | 7 4 |
| E | 88.2 | 99.0 | 3.10 | 4 14 | 6 36 |

| Brand.[a] | Tensile strength[b]—kilograms per square centimeter. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Neat cement. | | | | Mortar 1:3. | | | |
| | 1 day. | 7 days. | 28 days. | 60 days. | 1 day. | 7 days. | 28 days. | 60 days. |
| A | 24.8 | 41.8 | 48.1 | 47.3 | 7.0 | 16.8 | 23.4 | 25.3 |
| B | 23.6 | 43.5 | 45.7 | 45.7 | 7.0 | 17.5 | 21.7 | 22.8 |
| C | 23.2 | 41.2 | 47.8 | 45.3 | 9.3 | 19.8 | 26.7 | 30.1 |
| D | 24.5 | 44.5 | 50.7 | 47.5 | 8.7 | 20.8 | 28.8 | 30.9 |
| E | 27.3 | 44.2 | 51.3 | 50.6 | 10.8 | 23.2 | 28.5 | 29.1 |

[a] Brand *F*, without any addition of calcium sulphate, was quick-setting; consequently no test was made on the original material.

[b] Each result is the average of six briquettes. United States Government specifications were followed.

TABLE II.—*Physical tests of cements as received*—Continued.

| Brand.[a] | Tensile strength—pounds per square inch. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Neat cement. | | | | Mortar 1:3. | | | |
| | 1 day. | 7 days. | 28 days. | 60 days. | 1 day. | 7 days. | 28 days. | 60 days. |
| A | 353 | 595 | 685 | 673 | 100 | 238 | 333 | 360 |
| B | 337 | 617 | 651 | 649 | 100 | 248 | 308 | 325 |
| C | 330 | 586 | 679 | 644 | 133 | 282 | 380 | 428 |
| D | 348 | 633 | 722 | 677 | 124 | 294 | 409 | 441 |
| E | 388 | 628 | 731 | 720 | 154 | 331 | 407 | 414 |

[a] Brand *F*, without any addition of calcium sulphate, was quick-setting; consequently no test was made on the original material.

The plaster of Paris contained 55.88 per cent sulphuric anhydride. Each cement was analyzed, and the approximate amount of plaster necessary to give a certain percentage of sulphuric anhydride was calculated. The two substances were then placed in a ball mill and thoroughly mixed. In the case of sample *F* the clinker was crushed to pass a 20-mesh sieve, mixed with the plaster, and ground to the fineness indicated in Table III. This table shows the effect of sulphuric anhydride content on the setting time and on the tensile strength for various periods up to ninety days.

The results in Table III are not entirely uniform; however, as the results were obtained from more than 1,000 briquettes, general conclusions can be based on averages as follows:

*Setting time.*—In conformity with the results, already mentioned, of other investigations with calcium sulphate, most of the cements show a maximum retardation with 2 per cent or less of sulphuric anhydride and a shorter setting time with a higher or lower percentage.[13] In general, the initial-set curve obtained by plotting the percentage of sulphuric anhydride against the time is parallel to the final-set curve for the same cement.

[13] Calcium chloride, sodium sulphide, and several other electrolytes have somewhat the same effect. [See Carpenter, R. C., *Eng. Rec.* (1904), 50, 769. Witt, J. C., *This Journal, Sec. A* (1916), 11, 273.]

TABLE III—*Influence of sulphuric anhydride content on the tensile strength and setting time of cements.*[a]

| Cement. | Sulphuric anhydride ($SO_3$). | Specific gravity. | Setting time. | | Fineness. | | Tensile strength[b]—kilograms per square centimeter. | | | | | | | Tensile strength—pounds per square inch. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Neat cement. | | | | Mortar 1:3. | | | Neat cement. | | | | Mortar 1:3. | | |
| | | | Initial. | Final. | 100-mesh. | 200-mesh. | 1 day. | 7 days. | 28 days. | 90 days. | 7 days. | 28 days. | 90 days. | 1 day. | 7 days. | 28 days. | 90 days. | 7 days. | 28 days. | 90 days. |
| | *P. ct.* | | *H. m.* | *H. m.* | *P. ct.* | *P. ct.* | | | | | | | | | | | | | | |
| Brand A | 1.08 | 3.10 | 3 10 | 6 30 | 98.2 | 85.8 | 27.5 | 37.0 | 44.3 | 52.2 | 15.9 | 20.0 | 26.5 | 391 | 527 | 630 | 743 | 226 | 285 | 377 |
| | 1.52 | 3.10 | 4 15 | 7 55 | 97.6 | 85.6 | 27.6 | 40.2 | 45.5 | 51.8 | 15.2 | 19.9 | 25.5 | 393 | 573 | 648 | 738 | 216 | 283 | 364 |
| | 2.19 | 3.09 | 4 15 | 7 50 | 98.0 | 86.6 | 25.3 | 35.6 | 44.4 | 52.2 | 13.0 | 21.5 | 27.4 | 360 | 506 | 631 | 743 | 188 | 309 | 390 |
| | 2.81 | 3.09 | 3 10 | 6 20 | 98.4 | 87.0 | 21.4 | 29.4 | 43.7 | 48.5 | 9.9 | 17.6 | 24.2 | 305 | 418 | 623 | 690 | 142 | 250 | 345 |
| | 9.18 | 3.06 | 3 0 | 6 0 | 97.2 | 83.2 | 24.6 | 32.6 | 41.6 | 49.9 | 9.9 | 13.8 | 15.9 | 350 | 465 | 593 | 697 | 142 | 197 | 226 |
| Brand B | 1.14 | 3.06 | 3 40 | 6 25 | 99.2 | 85.2 | 28.5 | 40.0 | 43.0 | 42.2 | 15.0 | 21.1 | 23.4 | 407 | 569 | 612 | 600 | 213 | 300 | 333 |
| | 1.59 | 3.05 | 3 35 | 6 25 | 99.0 | 84.0 | 32.4 | 37.5 | 40.8 | 41.1 | 14.8 | 19.8 | 19.8 | 462 | 535 | 580 | 584 | 206 | 282 | 281 |
| | 1.89 | 3.05 | 3 35 | 6 30 | 98.2 | 82.8 | 30.5 | 38.8 | 43.1 | 44.6 | 18.8 | 24.4 | 25.1 | 435 | 553 | 613 | 635 | 268 | 347 | 358 |
| | 4.55 | 3.04 | 3 35 | 6 25 | 97.6 | 81.0 | 25.0 | 35.7 | 41.1 | 43.0 | 9.5 | 16.7 | 27.0 | 358 | 509 | 584 | 613 | 136 | 238 | 385 |
| | 9.92 | 3.01 | 3 30 | 6 25 | 97.0 | 82.8 | 24.1 | 36.6 | 42.3 | 45.5 | 10.0 | 13.0 | 11.9 | 344 | 523 | 602 | 648 | 143 | 187 | 170 |
| Brand C | 1.34 | 3.16 | 4 32 | 7 16 | 99.0 | 89.6 | 23.2 | 41.2 | 47.7 | | 19.8 | 26.7 | | 330 | 586 | 679 | | 282 | 380 | |
| | 2.10 | 3.12 | 4 5 | 7 10 | 98.6 | 88.4 | 26.2 | 37.5 | 45.7 | 44.7 | 17.0 | 24.7 | 28.7 | 374 | 536 | 650 | 636 | 241 | 351 | 409 |
| | 3.02 | 3.11 | 3 55 | 6 50 | 98.6 | 88.8 | 22.2 | 34.7 | 43.6 | 48.2 | 15.0 | 24.2 | 29.9 | 316 | 495 | 620 | 687 | 213 | 346 | 426 |
| | 4.86 | 3.09 | 5 30 | 7 35 | 98.6 | 91.0 | 22.8 | 29.2 | 40.0 | 50.0 | 9.0 | 13.0 | 12.7 | 325 | 416 | 569 | 711 | 128 | 187 | 182 |
| | 9.54 | 3.07 | 4 30 | 7 5 | 98.8 | 89.8 | 21.1 | 27.9 | 34.5 | 45.4 | 7.9 | 11.9 | 17.1 | 301 | 398 | 491 | 646 | 112 | 170 | 244 |
| Brand D | 1.34 | 3.10 | 4 26 | 7 4 | 98.6 | 85.6 | 24.4 | 44.5 | 50.7 | | 20.7 | 28.7 | | 348 | 633 | 722 | | 294 | 409 | |
| | 2.14 | 3.10 | 5 20 | 7 15 | 97.8 | 85.2 | 28.0 | 46.7 | 44.2 | 46.4 | 18.7 | 27.2 | 30.2 | 399 | 665 | 629 | 661 | 267 | 387 | 430 |
| | 3.30 | 3.09 | 5 10 | 6 0 | 97.6 | 84.6 | 26.2 | 45.5 | 47.6 | 51.5 | 18.3 | 28.0 | 32.8 | 373 | 648 | 678 | 733 | 261 | 399 | 469 |
| | 5.00 | 3.08 | 5 20 | 5 55 | 97.8 | 84.4 | 23.5 | 31.9 | 40.2 | 44.1 | 11.3 | 19.8 | 33.0 | 336 | 455 | 572 | 628 | 161 | 282 | 470 |
| | 10.20 | 3.04 | 4 0 | 6 30 | 98.0 | 84.6 | 21.3 | 29.8 | 38.9 | 45.2 | 10.4 | 14.9 | 22.9 | 302 | 425 | 553 | 644 | 149 | 213 | 229 |

| | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Brand E | 1.24 | 3.10 | 4 | 14 | 6 | 36 | 99.0 | 88.2 | 27.2 | 44.2 | 51.4 | ...... | 23.2 | 28.6 | ...... | 388 | 628 | 731 | ...... | 331 | 407 | ...... |
| | 2.05 | 3.08 | 4 | 55 | 6 | 30 | 98.0 | 86.8 | 31.5 | 44.3 | 46.6 | 44.9 | 19.4 | 26.9 | 28.0 | 449 | 631 | 664 | 639 | 276 | 384 | 399 |
| | 2.73 | 3.08 | 3 | 50 | 6 | 30 | 98.0 | 87.6 | 33.3 | 48.6 | 44.4 | 52.7 | 23.1 | 36.3 | 31.0 | 475 | 692 | 632 | 751 | 329 | 375 | 443 |
| | 4.79 | 3.07 | 3 | 50 | 6 | 10 | 98.6 | 88.4 | 26.7 | 32.6 | 37.2 | 46.5 | 12.8 | 28.6 | 38.0 | 381 | 465 | 531 | 662 | 184 | 408 | 512 |
| | 9.58 | 3.01 | 3 | 35 | 5 | 55 | 98.0 | 89.2 | 27.0 | 28.3 | 36.2 | 42.1 | 9.6 | 11.3 | 10.7 | 386 | 403 | 517 | 599 | 137 | 162 | 154 |
| Brand F | 1.46 | 3.10 | 4 | 20 | 8 | 0 | 99.0 | 88.0 | 29.0 | 45.7 | 44.1 | 42.3 | 15.2 | 22.2 | 25.3 | 414 | 650 | 628 | 603 | 217 | 316 | 361 |
| | 2.00 | 3.10 | 4 | 5 | 7 | 40 | 92.4 | 74.4 | 34.3 | 53.8 | 57.0 | 58.3 | 12.7 | 18.8 | 22.2 | 489 | 768 | 814 | 831 | 181 | 268 | 317 |
| | 3.59 | 3.10 | 3 | 10 | 6 | 25 | 88.8 | 79.0 | 34.3 | 47.3 | 50.0 | 55.1 | 16.4 | 23.2 | 27.3 | 489 | 674 | 713 | 785 | 233 | 330 | 389 |
| | 5.00 | 3.09 | 2 | 55 | 6 | 10 | 94.2 | 84.0 | 31.9 | 39.6 | 45.5 | 43.7 | 13.5 | 23.3 | 28.5 | 455 | 421 | 648 | 623 | 194 | 331 | 407 |
| | 9.11 | 3.06 | 2 | 20 | 5 | 15 | 95.4 | 86.2 | 21.9 | 21.9 | 34,3 | 38.9 | 10.9 | 22.3 | 30.2 | 312 | 335 | 489 | 554 | 157 | 317 | 430 |

[a] Soundness tests were made on each mix and found satisfactory.

[b] Each result shown here is the average of five briquettes.

*Tensile strength.*—When 1.50 to 2.00 per cent sulphuric anhydride has been added, the strength both in neat and mortar decreases with increase of the substance. Four of the cements show a maximum strength with approximately 1.50 per cent sulphuric anhydride, while two show a maximum with about 2 per cent. The 90-day briquettes develop maximum strength with a higher percentage of sulphuric anhydride than do the briquettes for the shorter periods. Additional neat and mortar briquettes have been made for periods ranging from six months to five years. No final conclusions can be drawn until the long-time tests are available. In making the calculations, the strengths of briquettes made with the cements as received were taken as 100 per cent,[14] and the comparison of results were made on the basis of the percentage loss in tensile strength. The percentage loss in strength caused by placing plaster equivalent to about 10 per cent of sulphuric anhydride in each cement was then studied. The following points become apparent:

1. With one exception, the percentage loss is greater with mortar briquettes than with the corresponding neat briquettes.
2. As the age of the neat briquettes increases from seven days, the percentage loss decreases. No definite conclusions can be drawn from the results of the mortar briquettes at present.
3. No relationship between the chemical composition of the cements and the effect of sulphate is apparent.

## INFLUENCE ON STORAGE FACTORS

It often happens that a cement is satisfactory at the time of manufacture, but becomes quick-setting or develops some other fault during storage. These alterations may take place gradually over a period of several weeks, or in as many days. Some writers are of the opinion that there is some relation between these changes and the sulphuric anhydride content. Acceleration tests have been devised to determine in advance some of the changes that may take place in cement during storage. One such test is to spread the cement in thin layers exposed to the moisture and carbon dioxide of the air and test from time to time for soundness and setting time.[15] A test recommended by Hentschel[16] is as follows: Two hundred grams of cement

[14] Brand *F* was quick-setting as received; so a sample containing 1.46 per cent sulphuric anhydride was taken as the standard.

[15] *This Journal, Sec. A* (1911), 6, 207.

[16] Hentschel, G., *Tonind.-Zeitg.* (1912), 36, 557.

are placed in a large Erlenmeyer flask; carbon dioxide, washed in sulphuric acid and in water, is passed into the flask for ten minutes. The contents of the flask are then shaken violently. This process is repeated three times. If the setting time of the cement becomes less than one hour, it is likely to deteriorate during storage. The latter test was applied to a number of samples of brand *F* chosen at random and to brands *A* to *E* for comparison. The results are shown in Table IV.

TABLE IV.—*Effect of carbon dioxide absorption on the setting times of cements.*

| Brand. | Sulphuric anhydride. | Original cement. | | | | After absorption of $CO_2$ for ten minutes. | | | | After absorption of $CO_2$ for twenty minutes. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Loss on ignition. | Water used. | Time of setting. | | Loss on ignition. | Water used. | Time of setting. | | Loss on ignition. | Water used. | Time of setting. | |
| | | | | Initial. | Final. | | | Initial. | Final. | | | Initial. | Final. |
| | *P. ct.* | *P. ct.* | *P. ct.* | *H. m.* | *H. m.* | *P. ct.* | *P. ct.* | *H. m.* | *H. m.* | *P. ct.* | *P. ct.* | *H. m.* | *H. m.* |
| A | 0.67 | 2.67 | 24 | 5 15 | 8 40 | 2.85 | 24 | 5 20 | 7 40 | 3.28 | 24 | 3 45 | 6 50 |
| B | 0.86 | 3.07 | 23 | 5 10 | 8 40 | 3.10 | 23 | 5 30 | 7 50 | 3.75 | 25 | 3 45 | 7 0 |
| C | 1.34 | 2.06 | 25 | 5 30 | 8 40 | 2.10 | 25 | 5 15 | 8 5 | 2.58 | 25 | 4 40 | 8 0 |
| D | 1.34 | 1.36 | 23 | 3 40 | 6 40 | 1.56 | 24 | 5 20 | 9 50 | 1.59 | 24 | 5 5 | 9 35 |
| E | 1.24 | 2.11 | 23 | 4 50 | 8 0 | 2.18 | 23 | 4 35 | 7 0 | 3.11 | 23 | 3 30 | 6 45 |
| F | 2.00 | 2.60 | 22 | 1 55 | 3 45 | 3.06 | 22 | 0 7 | 3 10 | 3.21 | 24 | 1 20 | 4 10 |
| F 1 | 1.50 | 2.13 | 22 | 2 35 | 5 50 | 2.30 | 23 | 1 50 | 5 40 | 2.37 | 25 | 3 5 | 5 50 |
| F 2 | 1.20 | 2.89 | 25 | 5 5 | 7 45 | 3.07 | 26 | 4 25 | 8 5 | 3.16 | 26 | 4 35 | 8 15 |
| F 3 | 1.41 | 3.80 | 25 | 4 10 | 7 20 | 4.03 | 25 | 4 35 | 10 0 | 4.19 | 26 | 5 15 | 9 45 |

[a] All samples were tested for soundness and found satisfactory.

In these examples it can be seen that there is no relation between the amount of sulphuric anhydride present and the change in setting time caused by absorption of carbon dioxide. The sample of brand *F* having the highest percentage of sulphuric anhydride is the only one that becomes quick-setting.

According to Hentschel[17] the change in setting time of a cement in storage is due to the formation of alkaline carbonates from absorption of carbon dioxide. The cements shown in Table IV were gauged with sodium carbonate solutions of three concentrations. It can be seen from Table V that the set was but little affected.

[17] Loc. cit.

TABLE V.—*Effect of sodium carbonate on the setting time of cements.*

| Brand. | Sulphuric anhydride ($SO_3$). | 4 grams per liter. Volume of solution per 100 grams of cement. | 4 grams per liter. Time of setting. Initial. | 4 grams per liter. Time of setting. Final. | 10 grams per liter. Volume of solution per 100 grams of cement. | 10 grams per liter. Time of setting. Initial. | 10 grams per liter. Time of setting. Final. | 20 grams per liter. Volume of solution per 100 grams of cement. | 20 grams per liter. Time of setting. Initial. | 20 grams per liter. Time of setting. Final. | 40 grams per liter. Volume of solution per 100 grams of cement. | 40 grams per liter. Time of setting. Initial. | 40 grams per liter. Time of setting. Final. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *cc.* | *H. m.* | *H. m.* | *cc.* | *H. m.* | *H. m.* | *cc.* | *H. m.* | *H. m.* | *cc.* | *H. m.* | *H. m.* |
| A | 0.67 | 24 | 5 20 | 9 25 | 24 | 5 40 | 9 0 | 24 | 4 20 | 8 40 | 24 | 4 15 | 7 45 |
| B | 0.86 | 23 | 5 50 | 9 50 | 23 | 5 35 | 9 0 | 23 | 5 25 | 8 25 | 23 | 5 0 | 8 15 |
| C | 1.34 | 25 | 5 45 | 9 50 | 25 | 5 30 | 9 25 | 25 | 5 0 | 8 40 | 25 | 4 45 | 8 15 |
| D | 1.34 | 23 | 3 50 | 5 55 | 23 | 3 5 | 6 5 | 23 | 1 50 | 5 0 | 23 | 1 0 | 4 20 |
| E | 1.24 | 23 | 5 45 | 8 15 | 23 | 3 40 | 7 50 | 23 | 4 0 | 7 30 | 23 | 2 45 | 5 30 |
| F 1 | 1.50 | 22 | 2 10 | 5 45 | 22 | 2 5 | 5 35 | 22 | 1 50 | 5 20 | 22 | 2 15 | 6 15 |
| F 2 | 1.20 | 26 | 5 5 | 8 0 | 26 | 4 10 | 7 50 | 26 | 4 5 | 7 30 | 26 | 3 10 | 7 15 |
| F 3 | 1.41 | 25 | 4 55 | 7 55 | 25 | 4 0 | 7 50 | 26 | 4 0 | 6 55 | 26 | 3 0 | 7 20 |

## SUMMARY

The following statements concerning the quantity of sulphuric anhydride in cement are based on the cements studied in this laboratory for periods [18] up to ninety days:

1. The maximum retardation of set is produced by 1.5 per cent to 2 per cent.

2. In general, the briquettes show a decrease in strength when the cement contains more than 2 per cent, except in brands *E* and *F*, which decrease in strength only when the content amounts to about 5 per cent.

3. The soundness (five hours in steam) is unaffected by any amount investigated.

4. The percentage loss in tensile strength is greater with the mortar than with the neat briquettes.

[18] Measurements of expansion bars are being made over a period of months, and briquettes for long-time tensile-strength tests are being matured. Those that have been since completed indicate no well-defined relation between tensile strength and sulphuric anhydride content, but show that, in general, the maximum strength of the mortar briquettes corresponds to a higher percentage of this compound than in the series discussed in this paper. With most of the cements investigated, sulphuric anhydride, in quantities less than 3 per cent, caused no serious expansion in sea water.

5. The percentage loss in tensile strength of the neat briquettes decreases as the age increases from seven days.

6. No relation between the sulphuric anhydride content of a cement and the effect of exposure to carbon dioxide is apparent.

7. Results indicate that the formation of alkali carbonates is not an important factor in the change of the physical properties of cement during storage.

149517——3

# THE RADIOACTIVITY OF PHILIPPINE WATERS *

By J. R. WRIGHT [1] and GEORGE W. HEISE

*(From the Bureau of Science, Manila)*

ONE PLATE AND TWO TEXT FIGURES

In recent years there have been so many investigations of the radioactivity of waters that comparative data are now available from many parts of the world. It is the purpose of this paper to present the results of similar work on the radioactivity of typical Philippine waters.[2]

Up to the present time our work on radioactivity has been limited to the determination of radium emanation and actual radium content of typical springs and deep, drilled wells. As yet, no attempt has been made to study the radioactivity of the deposits or residues from springs, or of typical rocks, or of the gases evolved from springs or wells. All of the work was done on Luzon, most of it in Mountain and Laguna Provinces. The majority of the places visited are shown on the accompanying maps (figs. 1 and 2).

The geography and the geology of the country in and around Baguio have been described by Eveland,[3] and of the remainder of Mountain Province by Smith.[4]

Owing to the difficulties of travel, equipment for provincial expeditions had to be reduced to a minimum; in consequence comparatively few data on the chemical composition of the waters were secured.

## EXPERIMENTAL PART

The testing apparatus was one of the Spindler and Hoyer aluminum leaf electroscopes used in previous radioactive meas-

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[2] The only previous attempt to determine the radioactivity of Philippine waters was made by R. F. Bacon [*This Journal, Sec. A* (1910), 4, 267–280], but his results were only qualitative, being obtained under conditions which made even approximately accurate results impossible.

[3] Eveland, A. J., Notes of the geology and geography of the Baguio mineral district, ibid., *Sec. A* (1907), 2, 207–233.

[4] Smith, Warren D., Notes on a geologic reconnaissance of Mountain Province, Luzon, P. I., ibid., *Sec. A* (1915), 10, 177–209.

urements [5] in the Philippines. The instrument was provided with the usual equipment of tripod, shaking vessel, and circulation system necessary for field work (Plate I, fig. 1).

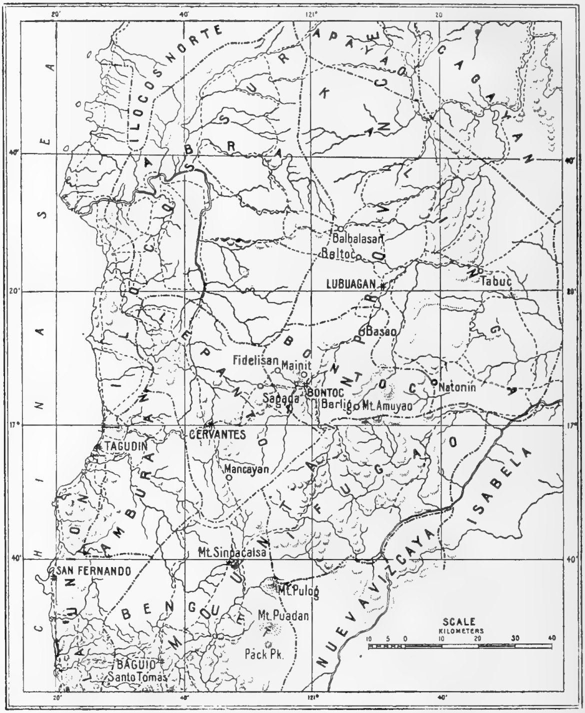


FIG. 1. A part of northern Luzon.

Because of the high humidity generally encountered in the Philippines, a small tube of calcium chloride was fastened inside the leaf chamber of the electroscope. In all determinations, in the field or in the laboratory, a calcium chloride tube (gen-

[5] Wright, J. R., and Smith, O. F., *Physik. Zeitschr.* (1914), **15**, 31–39; *This Journal, Sec. A* (1914), **9**, 51–77; *Phys. Rev.* (1915), n. s. **5**, 459–482; (1916), n. s. **7**, 49–61.

erally of the Bender and Hobein type) was introduced into the circulation system, so that all air and gases were dried before they entered the ionization chamber. It was found impossible

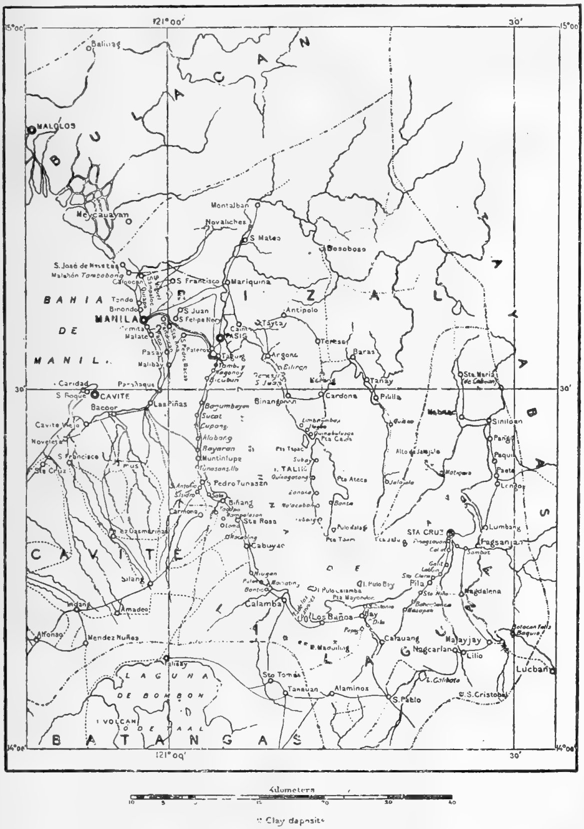

FIG. 2. South-central Luzon.

to obtain reliable readings without this precaution. Our results indicated that drying is also necessary at lower temperatures in order to ensure correct results with the type of instrument

used. With the precautions noted, the natural leak of the instrument was usually lower in laboratory work, and frequently lower in field work, than the figures for the natural leak furnished by the instrument makers. The electroscope was charged by means of a bank of storage cells in the laboratory; in the field, by means of an ebonite rod.

*Standardization of instrument.*—The electroscope was standardized by means of a radium bromide solution of known strength furnished for this purpose by the Bureau of Standards, Washington, D. C. A definite portion of this solution was kept sealed in a proper vessel (essentially a "Curie tube"[6]) for over one month. The emanation was then removed from the solution by boiling and by circulation of air and was drawn into the evacuated ionization chamber. The arrangement of the apparatus is shown graphically in Plate I, fig. 2.

A determination was conducted as follows: After the instrument had been charged, it was allowed to stand until the leak had become small and nearly constant. Readings both of the natural leak and of the leak due to emanation content were taken at intervals of five minutes, as measured by a stop watch, and were estimated to tenths of a division on the telescope scale.

The sealed vessel *B*, containing the acidulated sample to be tested, was heated in a water bath *F* to about 90° C. Little danger of breakage was incurred by this procedure, because the vessels had been heated to about the same temperature before being sealed. The ionization chamber *A* was evacuated by means of an electrically driven Geryk oil pump *D*. A manometer *E* was attached, in order to measure the pressure in the chamber and to detect leaks in the joints of the tubing or in the ionization chamber. When a vacuum had been secured, the stopcock *H* leading to the pump was closed. As the ends of the glass aspirator tubes had been drawn to a point and notched with a file, slight pressure with the fingers at *M* was sufficient to break off the point of the delivery tube inside the rubber tubing, thus allowing the vapors and gases from the vessel *B* to pass slowly through the (calcium chloride) drying tube *C* and into the evacuated ionization chamber. Under the decreased pressure, the liquid in the flask *B* boiled readily, and all of the emanation was rapidly drawn into the ionization chamber. In order to remove the last traces of emanation, the point of the

[6] Curie, P., Dosage du radium par la mesure de l'emanation dégagée, *Le Radium* (1910), **7**, 65–70.

glass tube entering the flask was broken off at $L$ and the flask was washed out with a current of air, regulated by means of a screw-stopcock $J$, until the pressure in the system had been equalized. The cock $I$ was then closed, and after fifteen minutes, readings of the leak were taken as described above.

The standardization was checked with a known quantity of standard radium-bromide solution put directly into the shaking vessel used in field determinations. After the closed vessel had been allowed to stand one month to ensure radioactive equilibrium, a determination was made by the usual field method. Two different determinations showed satisfactory agreement with each other and with the results previously obtained. This procedure is much simpler than the usual method of standardization, and since determinations both with the standard solution and with water samples of unknown activity are thus performed under identical conditions, the chance for error is minimized. Our data indicate that this method can be relied upon for accurate results.

*The field determination of radium-emanation content.*—The manner of taking water samples was, of course, dependent on the exigencies of travel and on the location and type of the source of the water to be examined. All reasonable precautions [7] necessary to secure representative samples without loss of emanation were observed. Whenever possible, the collecting can (shaking vessel) was dipped directly into the water to be examined; otherwise the water was allowed to flow directly into the can from the source (for example, a flowing well), or was transferred from the source in a second vessel and poured into the can. In all cases care was taken to prevent loss of emanation through shaking or aëration.

The method of taking samples was not free from objection in every instance, and sometimes, for example, when a spring emerged from the bed of a river or in the bottom of a large pool, it was found impossible to obtain a representative sample. However, we believe that with the exception of these cases the error due to the method of taking the sample did not affect appreciably the accuracy of the results.

The shaking method of Schmidt [8] was employed in field work. Determinations were made as soon as practicable after a sam-

[7] Engler, C., Sieveking, H., and Koenig, A., Neue Beiträge zur Messung der Radioaktivität von Quellen, *Chem. Zeitg.* (1914), **38**, 425–427.

[8] Schmidt, H. W., Über eine einfache Methode zur Messung des Emanationsgehaltes von Flüssigkeiten, *Physik. Zeitschr.* (1905), **6**, 561–566.

ple had been taken, usually within thirty minutes, and in no case after more than three hours. The arrangement of the apparatus is shown in Plate I, fig. 2.

The procedure in an ordinary field determination was as follows: The instrument was charged, and the natural leak was determined in the usual manner. The shaking can, containing a fresh-water sample, was then held vertically and open, until the water had drained to the level of the lower stopcock. The can was then closed, vigorously shaken for about one minute, and placed in the circulatory system as shown in Plate I. The air and the emanation in the system were circulated by means of a small rubber bulb for two minutes to ensure equal distribution of the emanation. The stopcocks on the ionization chamber were then closed, and fifteen minutes later the leak was determined, as previously described.

*Determination of radium content.*—Samples of typical waters were brought to the laboratory, sealed in proper vessels, allowed to stand for a month, and tested for radium content. The method of procedure was identical with that described with the standard solution, except that 400 cubic centimeter Jena flasks, equipped with aspirator tubes, were used to hold the water instead of the tube used for the radium solution. About 250 cubic centimeters of water were used in a determination. In some cases, when larger quantities of water were available, as much as 15 liters were evaporated to 250 cubic centimeters, acidified with hydrochloric acid, sealed in Jena flasks, and tested.

*Calculation of results.*—Radium-emanation content was calculated in terms of the weight of radium that would produce the leak noted when in radioactive equilibrium with its own emanation, and is expressed as grams $\times 10^{-12}$ per liter of water.

The apparatus constant was calculated from the formula [9]

$$a=\frac{1000}{w}\cdot\frac{l_1+l_2+l_3}{l_3}\left(1+\alpha\frac{w}{l_1}\right) \qquad (1)$$

in which

$w$ is the quantity of water, in cubic centimeters, under investigation;

$l_1$, $l_2$, and $l_3$ are the quantities of air (in cubic centimeters) in the shaking vessel, in the respiration system, and in the ionization chamber, respectively; and

$\alpha$ is the fraction of the emanation remaining in the water after shaking.

[9] Schmidt, H. W., op. cit., 565.

The radioactivity of any water expressed in grams of radium may be then readily calculated from the formula

$$m^1 = a\, m\frac{Z'}{Z} \qquad (2)$$

in which

$a$ is the constant derived from (1);

$Z$ is the leak caused by $m$ grams of radium (determined with the standard solution); and

$Z'$ is the leak caused by the emanation from the water in question.

Since it was not practicable, especially in the field, to wait the three hours necessary for the leak due to emanation to reach maximum value, readings were taken, as previously mentioned, fifteen minutes after filling the ionization chamber, and the maximum leak was calculated by means of a radium-emanation decay curve.

For use in the above equation the readings for the leak ($Z$ and $Z'$) were reduced by means of a calibration curve from divisions of the telescope scale to volts, and the natural leak of the instrument was in each case subtracted from the leak observed with emanation in the ionization chamber.

*Limits of accuracy and probable error.*—Although the object of this work was primarily to get reliable comparative data rather than exceedingly accurate absolute values, it is probable that the error was not great. The radium solution used for standardization may be considered accurate within 5 per cent. Duplicate determinations made with the standard solution checked within 1.5 per cent. Duplicate determinations made in the field on the same water checked within the limits of observational error. We have reason to believe that, except for the isolated cases noted in which proper samples could not be secured because of the nature of the source, the maximum error in field determinations was not greater than 7 per cent. Therefore the probable error was much smaller and hence was well within the limits of accuracy to be expected for this class of work.

*The radium-emanation content of Philippine waters.*—No attempt was made in the field to determine anything but radium-emanation content. That we were actually dealing with radium emanation was shown by the fact that when the gases from a number of waters studied were allowed to remain in the ionization chamber for long periods of time the typical decay curve of the radium emanation was obtained.

The radioactivity of the Philippine waters examined is shown in Table I.

TABLE I.—*Radioactivity of Philippine waters.*

[Sources having reputations for medicinal or healing properties are designated by a *.]

| No. | Date. | Province, town, and barrio. | Source. | Geologic formation. [a] | Radium emanation per liter. [b] Grams x $10^{12}$. | Remarks. |
|---|---|---|---|---|---|---|
| | 1916. | | | | | |
| 1 | June 7 | Batangas, Batangas | Artesian well 686 | | 2,106 | Nonthermal. |
| 2 | June 6 | do | Crater lake, Taal Volcano | Volcanic sinter | (c) | |
| 3 | June 10 | Bulacan, Marilao | Artesian well * | | neg. | Do. |
| 4 | Apr. 9 | Bulacan, San Miguel de Mayumo, Sibul Springs. | Sibul Springs * | Limestone | 1,284 | Nonthermal, mildly sulphureted. |
| 5 | June 9 | do | do | do | 1,293 | Do. |
| 6 | June 28 | Laguna, Bay | Artesian well at municipio | | neg. | Nonthermal. |
| 7 | do | do | Artesian well | | trace | Do. |
| 8 | Apr. 20 | Laguna, Calamba, Bucal | Bucal Spring [d] | Brecciated conglomerate | 41 | Large nonthermal spring. |
| 9 | do | Laguna, Calamba, Pansol | Pansol Springs * | Volcanic basalt | neg. | Series of large hot and cold springs. Sample from cool portion (31° C.). |
| 10 | June 11 | do | do | do | neg. | Sample from hot portion (45° C.). |
| 11 | June 25 | Laguna, Lilio | San Mateo Spring | Conglomerate | 430 | Temperature 23° C. |
| 12 | Apr. 19 | Laguna, Los Baños | Hot spring near sanitarium * | Igneous conglomerate cemented by tuff. | 539 | Temperature 70° C.; probably from same source as water for sanitarium. |
| 13 | June 29 | Laguna, Majayjay, Olla | Olla Spring | Loose volcanic agglomerate | 528 | Temperature 22° C.; probably seepage from a river in vicinity. |
| 14 | do | Laguna, Majayjay, Malinao | Sinabac Spring | Igneous conglomerate | 1,297 | Temperature 25° C. |
| 15 | June 24 | Laguna, Nagcarlan | San Diego Spring * | do.? | 526 | Do. |
| 16 | June 25 | do | San Vicente Spring | do.? | 317 | Temperature 21.5° C. |
| 17 | do | Laguna, Nagcarlan, Bubuy (?) | Buenaventura Spring | do.? | 426 | Temperature 22° C. |
| 18 | June 30 | Laguna, Paete | Small spring | Igneous conglomerate | 496 | Temperature 25° C. |

| | | | | | | |
|---|---|---|---|---|---|---|
| 19 | Apr. 21 | Laguna, Pagsanjan | Large artesian well | | 501 | Temperature 31° C. |
| 20 | Apr. 22 | do | Spring and well | | 124 | Temperature 33.5° C. |
| 21 | Apr. 21 | Laguna, Pagsanjan, Maulauin | Small artesian well | | 880 | Temperature 32° C. |
| 22 | do | Laguna, Pagsanjan, Pinagsanjan | Bumbungan Spring [d] | | 146 | Temperature 31° C. |
| 23 | ne 30 | Laguna, Pakil | Baño Spring | Igneous conglomerate | 365 | Temperature 25.5° C. |
| 24 | June 22 | Laguna, San Pablo | Bañadero Spring | | 713 | Nonthermal. |
| 25 | do | Laguna, San Pablo, Cabunsud | Municipal spring | | trace | Do. |
| 26 | June 23 | Laguna, San Pablo, Maganpun | Ansaran Spring | | 517 | Do. |
| 27 | do | do | Baño Spring | | 606 | Do. |
| 28 | do | Laguna, San Pablo, San Gabriel | Pansol (?) Spring | | 293 | Do. |
| 29 | do | do | Ylang-ylang (?) Spring | | 456 | Do. |
| 30 | June 24 | Laguna, San Pablo, San Lucas | Spring on Malinao River bank | | 391 | Do. |
| 31 | do | do | Majaban bato Spring | | 448 | Nonthermal; situated on shore of San Pablo Lake. |
| 32 | June 22 | Laguna, San Pablo, Santa Maria | Años Spring [a] | | 324 | Temperature about 40° C.; located in bed of Añosan River; sample probably mixed with river water. |
| 33 | June 30 | Laguna, Santa Cruz | Small artesian well | | 131 | Nonthermal; located on plaza. |
| 34 | do | do | Large artesian well 459 (?) | | nil | Temperature 36° C. |
| 35 | May 30 | La Union, San Fernando | Municipal spring | Andesite | 242 | Nonthermal. |
| 36 | June 1 | La Union, Santo Tomas | Artesian well | | trace | Do. |
| 37 | Apr. 15 | Manila | Municipal supply | Limestone | nil | From service tap. |
| 38 | do | Manila (Philippine General Hospital). | Drilled well (pumping) | | nil | |
| 39 | May 20 | Mountain, Aoua | Spring at Kilometer 65 | | nil | Nonthermal; elevation, 1,200 meters. |
| 40 | do | do | Spring at Kilometer 76 | | nil | Nonthermal; elevation, 1,250 meters. |

[a] Most of the data in this column were secured from V. E. Lednicky, chief, division of mines, Bureau of Science.

[b] When there was no change in the leak when radioscope was filled with gas, emanation content is designated as "nil;" when the increase was so slight that its magnitude was uncertain, emanation content is designated as "negligible" (neg.); when increase was positive, but too small to warrant calculation, emanation content is designated as "trace."

[c] Tested for radium content only. Negative results with 250 cubic centimeters.

[d] *Bucal* means "spring."

TABLE I.—*Radioactivity of Philippine waters*—Continued.

| No. | Date. | Province, town, and barrio. | Source. | Geologic formation. | Radium emanation per liter. Grams x $10^{12}$. | Remarks. |
|---|---|---|---|---|---|---|
| | 1916. | | | | | |
| 41 | May 1 | Mountain, Baguio | Spring, Antimok Valley | Andesite (?) | nil | Nonthermal; about 1 kilometer above Headwaters mine. |
| 42 | May 27 | do | Spring, Antimok Valley at Benguet Consolidated mine. | Andesite | 93 | Nonthermal; seepage elevation 820 meters. |
| 43 | May 1 | do | Spring, Antimok Valley at Headwaters mine. | Andesite and diorite, volcanic sinter overlying tuff. | nil | Nonthermal; seepage elevation 1,060 meters. |
| 44 | May 27 | Mountain, Baguio, Bua | Spring at Kilometer 5 | Decomposed andesite and diorite. | trace | Do. |
| 45 | Apr. 27 | do | City spring, Bokawkan Road | Andesite | 108 | Nonthermal; used for municipal supply, elevation 1,250 meters. |
| 46 | Apr. 29 | do | Camp John Hay, No. 1 spring | Igneous, fine-grained rock. | 194 | Nonthermal; supplies Camp John Hay, elevation 1,200 meters. |
| 47 | do | do | Camp John Hay; spring at ice plant. | do | 122 | Nonthermal. |
| 48 | May 26 | do | Dominican Hill spring | | 111 | Nonthermal; supplies Dominican building. |
| 49 | Apr. 28 | do | Federle's spring | Andesite | 137 | Nonthermal; located beyond Topside. |
| 50 | Apr. 26 | do | Government Center spring | Igneous, fine-grained rock. | 163 | Nonthermal; used for municipal supply. |
| 51 | do | do | Pakdal Spring | Andesite | trace | Nonthermal. |
| 52 | Apr. 27 | Mountain, Baguio | Sanitary camp spring | do | 29 | Do. |

| | | | | | | |
|---|---|---|---|---|---|---|
| 53 | May 17 | Mountain, Banaue | Spring near rest house | | 289 | Nonthermal; elevation 1,100 meters. |
| 54 | do | do | Small spring near schoolhouse | | 381 | Nonthermal; elevation 1,050 meters. |
| 55 | May 14 | Mountain, Bontoc | Spring near provincial stable | Andesite | trace | Nonthermal; elevation 850 meters. |
| 56 | do | do | Spring adjacent to municipal spring. | Volcanic tuff | neg. | Do. |
| 57 | May 13 | Mountain, Bontoc, Samoki | Spring, upstream | Quartz diorite | nil | Do. |
| 58 | do | do | Spring, downstream | do | neg. | Do. |
| 59 | May 10 | Mountain, Cervantes | Hot spring on river bank, opposite town. | Andesite | nil | Temperature 50° ±, elevation 770 meters. |
| 60 | May 9 | do | Municipal supply | Diorite and andesite | nil | From service tap. |
| 61 | do | Mountain, Cervantes, Comilias | Hot spring * | Andesite | nil | Temperature 45° ±, elevation 450 meters. |
| 62 | May 5 | Mountain, Haight's | Spring used for drinking | Andesite (?) | nil | Nonthermal; elevation 2,400 meters. |
| 63 | May 6 | do | Spring near barn | do | nil | Nonthermal; probably seepage. |
| 64 | Dec. 18 | Mountain, Itogon | Hot springs * | Andesite | nil | Temperature 45° ±. |
| 65 | Dec. 21 | Mountain, Itogon, Camp Lubang | do | Andesite and diorite | nil | Temperature 40° ±. |
| 66 | May 18 | Mountain, Kiangan | Spring supplying provincial building. | | 189 | Nonthermal, elevation 870 meters. |
| 67 | do | do | Spring near above | | trace | Do. |
| 68 | May 19 | do | Spring east of provincial building. | | 150 | Nonthermal; probably one spring with two outlets 820 meters. |
| 69 | do | do | Spring adjacent to above | | 150 | |
| 70 | do | do | Spring northeast of provincial building. | | 945 | Elevation 820 meters. |
| 71 | do | do | Spring east of school, on Nueva Vizcaya road. | | 1,058 | Nonthermal; sample could not be secured directly from source, but was taken from a small reservoir. |

TABLE I.—*Radioactivity of Philippine waters*—Continued.

| No. | Date. | Province, town, and barrio. | Source. | Geologic formation. [a] | Radium emanation per liter. Grams x $10^{12}$. | Remarks. |
|---|---|---|---|---|---|---|
| | 1916. | | | | | |
| 72 | May 29 | Mountain, Klondike | Klondike Springs * | Igneous conglomerate cemented by tuff. | neg. | Temperature 50°; from different springs of a series. |
| 73 | do | do | do | do | trace | |
| 74 | May 22 | Mountain, Loo | Small spring near rest house | | trace | Elevation 1,660 meters. |
| 75 | May 15 | Mountain, Mainit | Mainit Spring | Andesite; silicious and calcareous center. | nil | Sample from boiling saline spring; elevation 1,200 meters. |
| 76 | May 8 | Mountain, Mancayan | Spring on Balili trail | Trachyte andesite | 114 | Nonthermal; spring about 1 km. east of rest house; elevation 1,350 meters. |
| 77 | May 4 | Mountain, Mountain trail, Kilometer 30. | Spring on Atok trail | Andesite | nil | Nonthermal; elevation 1,650 meters; probably seepage. |
| 78 | do | do | Spring near rest house | do | nil | Do. |
| 79 | May 7 | Mountain, Mountain trail, Kilometer 88. | do | do | nil | Probably seepage; elevation, 2,050 meters. |
| 80 | May 11 | Mountain, Sagada | Mission spring | | 111 | Nonthermal; water supply for mission; elevation 1,600 meters. |
| 81 | do | do | Underground river | Limestone | trace | Elevation 1,400 meters. |
| 82 | May 12 | Mountain, Sagada, Tetepan | Small spring at slide | Decomposed andesite | 263 | Elevation 1,200 meters. |
| 83 | do | do | Barrio spring | Andesite and diorite | nil | Elevation 900 meters. |
| 84 | May 31 | Mountain, Tagudin | Artesian well, plaza | | trace | Tagudin artesian well waters are mildly sulphureted. |
| 85 | do | do | Artesian well; Calle Español | | 137 | Temperature about 35°C. |
| 86 | do | do | Dismantled artesian well near cemetery. | | 341 | Nonthermal. |

| | | | | | | |
|---|---|---|---|---|---|---|
| 87 | Dec. 16 | Mountain, Trinidad | Spring 100 meters west of presidencia. | Limestone | nil. | Probably a local spring. |
| 88 | May 29 | Pangasinan, Dagupan | Artesian well, Calle M. H. del Pilar. | | 78 | Sample secured by dipping, hence result is probably low. |
| 89 | do | do | Artesian well near church | | 91 | Do. |
| 90 | do | do | Artesian well, river bank | | neg. | Do. |
| 91 | June 19 | Rizal, Parañaque | Artesian well, plaza | | 632 | Do. |

*Radium content of Philippine waters.*—Samples of twenty typical waters, from which the emanation had been removed, were acidified, sealed up in proper containers, and allowed to stand at least one month. They were then tested for radium content, by the method previously outlined. In no case was there any indication of radioactivity.

In addition, 15 liters of Batangas water (No. 1), 15 liters of Los Baños water (No. 12), and 5 liters of Sibul Springs water (Nos. 4 and 5) were evaporated to small bulk and similarly tested. The first two showed no emanation, and the third showed a trace.

The radioactivity of the waters studied was, therefore, primarily due to emanation derived from the materials in the ground with which the water had been in contact and not to dissolved radium salts.

## DISCUSSION

The work has not proceeded sufficiently to justify many conclusions. The typical Philippine water supplies studied possess no abnormal features so far as their radioactivity is concerned. Though some of them are moderately high in radium-emanation content, none show an excessive amount, compared with waters from other countries reported in the literature.[10]

Since hot water is a poorer solvent of gases than cold water, it is to be expected that the radioactivity of hot springs should, in general, be low. With the exception of the Los Baños water (No. 12), most of the thermal waters studied in the course of this work showed little or no activity.[11]

In general, the average activity of igneous rocks is greater than that of the sedimentary,[12] and it is to be expected that water from the former material should show higher emanation content. Thus Sahlbom [13] found that the water from sedimentary deposits was much lower in activity than that from primary rocks; further, that wells bored in the acid rocks showed the highest activity. In the Philippines the relatively small number of de-

[10] Cf. Schlundt, H., *Bull. U. S. Geol. Surv.* (1909), **No. 395**, 31; *Journ. Phys. Chem.* (1914), **18**, 662. Isitani, D., *Proc. Tokyo Math. Physic. Soc.* (1912), and following years.

[11] The average temperature of ground waters in the lowlands of Luzon is about 28° C.

[12] Cf. Clarke, F. W., Data of geochemistry, *Bull. U. S. Geol. Surv.* (1916), **No. 616**, 122.

[13] Sahlbom, N., *Arkiv Kemi, Min. Geol.* (1915), **6**, No. 3, 1–52; through *Chem. Abst.* (1916), **10**, 1134.

terminations made and the frequent difficulty of determining the actual water-bearing stratum, since this is frequently not the same as the geological formation exposed at the place where the water emerges, make generalizations at this time inadvisable.

In some cases, at least, the radioactive material from which the water derived its activity must have been confined to a rather limited area. Thus it was pointed out [14] that Olla Springs (No. 13) were in reality only seepage water derived from a river about a hundred meters distant.[15] The "spring" water must, therefore, have acquired its activity in the course of a short journey underground.

So far as the available analytical data at hand are concerned, there is no apparent general relation between the chemical quality of the water and its radioactivity. According to Schlundt [16] there is, in general, no detectible difference in activity between acid and alkaline waters. Practically all of the waters tested at the source in the course of this work were acid to phenolphthalein and alkaline to methyl orange. We have been equally unable to make generalizations concerning other factors. This is not surprising, since the emanation content appears to be due not to dissolved radium but to contact with radioactive materials, sometimes within a very restricted area. For the sake of completeness, the available analyses of the waters under investigation, as compiled from the data in the Bureau of Science, are included in Table II.

There was no sharply defined rainy season [17] during 1916 in the places visited. With the exception of the determinations made in April and December, the tests for radioactivity were conducted during months of considerable rain.

Though no systematic study of the relation between the radioactivity and the variation of flowing wells and springs has been made,[18] it may be of interest to point out that Sibul Springs (Nos. 4 and 5) was tested on two different occasions—once in the middle of the dry season, that is, after two or three prac-

[14] By V. E. Lednicky, chief, division of mines, Bureau of Science.

[15] A bacteriological test made in the course of a field survey of water supplies confirmed this view.

[16] Schlundt, H., *Bull. U. S. Geol. Surv.* (1909), No. 395, 30.

[17] For the distribution of rainfall in the Philippines according to locality and season, see Cox, A. J., *This Journal, Sec. A* (1911), 6, 287–296.

[18] Many springs and deep wells whose flow varies greatly with the tide show no appreciable variation in chemical quality. See Heise, G. W., Note on the tidal variation of springs and deep wells in the Philippine Islands, *This Journal, Sec. A* (1916), 11, 125–127.

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TABLE II.—*Chemical analyses of waters tested for radioactivity.*

[L=little, Lw=low, N=nil, S=small, T=trace. Analytical results expressed as parts per million.]

| Source. | Province, town, barrio. | Capacity per minute. | Color. | Alkalinity (CaCO3). | Acidity (CO2). | Total solids. | Silica (SiO2). | Iron (Fe). | Calcium (Ca). | Magnesium (Mg). | Chlorine (Cl). | Carbonates (CO3). | Bicarbonates (HCO3). | Sulphates (SO4). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Liters.* | | | | | | | | | | | | |
| Artesian well | Batangas, Batangas | | | | | 380 | 68 | | 15 | 15 | 10 | | | 7 |
| Do | Bulacan, Marilao | large | | | N | | 29.6 | a 0.75 | 3.7 | T | 17.2 | 8.6 | 161.7 | 15.4 |
| Springs | Bulacan, Sibul | large | Nil | 380 | + | 550 | 15 | T | 148 | 14.3 | 32 | N | 463.6 | N |
| Artesian well | Laguna, Bay (Los Baños Road). | | Slight | 520 | 31 | 470 | 80 | 0.6 | 36 | 22 | 40 | N | 560 | |
| Do | Laguna, Bay (Presidencia) | | do | 640 | 33 | 720 | 85 | 0.83 | 93 | 34 | 30 | N | 760 | N |
| Spring | Laguna, Calamba, Bocal | large | | 190 | + | | | 0.17 | | | 39 | N | 240 | 24 |
| Hot spring | Laguna, Calamba, Pansol | large | | 210 | + | 850 | 135 | T | 39.3 | 19.6 | 250 | 10 | 256 | 37 |
| Cold spring | do | | | 220 | + | | | 0.33 | | | 66 | N | 277 | 26 |
| Spring | Laguna, Lilio, San Mateo | | | 93 | 34 | | | 0.1 | | | 8 | N | 120 | T |
| Hot spring | Laguna, Los Baños | 20 | Nil | 220 | 18 | 1,440 | 220 | 0.18 | 40 | 15 | 500 | N | 270 | 30 |
| Olla Spring | Laguna, Majayjay | large | | 56 | 18 | | | 0.25 | 17 | | 7 | N | 70 | T |
| Sinabac Spring | Laguna, Majayjay, Sinabac | large | | 46 | T | 100 | | 2.0 | 19 | | 7 | N | 30 | T |
| San Diego Spring | Laguna, Nagcarlan, San Diego. | large | | 130 | 64 | | | 0.1 | 60 | | 8 | N | 160 | 16 |
| San Vicente Spring | Laguna, Nagcarlan, San Vicente. | large | | 58 | 22 | Lw | | 0.1 | 14 | | 6 | N | 73 | 16 |
| Spring | Laguna, Paete | small | | 120 | 22 | | | 0.4 | 60 | | 8.8 | N | 150 | N-T |
| Bumbungan Spring | Laguna, Pagsanjan | large | | 170 | 40 | Lw | | N | | | 22 | N | 210 | T |
| Artesian well | do | 600 | | 260 | N | 742 | 72 | 1.1 | 14 | 26 | 170 | T | 100 | 55 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Do | Laguna, Pagsanjan, Maulauin. | 20 | | 154 | N | 402.5 | 80 | 0.1 | 21.5 | 8.7 | 41.2 | T | 187.1 | 24.7 |
| Well and spring | Laguna, Pagsanjan | | | 175 | N | | | N | | | 29 | T | 220 | 20 |
| Spring | Laguna, Pakil | large | | 120 | 19 | Lw | | 0.25 | | | 9 | N | 150 | T |
| Do | Laguna, San Pablo, Cabunsud. | large | Nil | 110 | 23 | S | | 0.07 | 21 | | 14 | N | 140 | 28 |
| Springs | Laguna, San Pablo, Pansol | small | | 210 | 59 | Lw | | 0.17 | | | 12 | N | 260 | 16 |
| Spring | La Union, San Fernando | large | Nil | 200 | | | | T-N | | | 25 | N (?) | 250 | 29 |
| Artesian well | La Union, Santo Tomas | | | 320 | N | 1,140 | 22 | 1.2 | L | 12 | 430 | T | 390 | T |
| Deep well | Manila (Philippine General Hospital). | | Nil | | | 555 | 69 | 0.4 | 9 | 2 | 44 | 10 | 400 | 10 |
| Government Center spring. | Mountain, Baguio | large | | 3 | + | | | N | | | 7 | N | 4 | 9 |
| City spring | Mountain, Baguio (Bokawkan Road). | large | | 67 | + | | | T | | | 5 | N | 84 | T |
| Sanitary camp spring. | Mountain, Baguio | small | | 13 | + | | | T | | | 5 | N | 160 | T |
| Spring | Mountain, Baguio, Camp John Hay. | large | | 7 | + | | | N | | | 4 | N | 9 | T |
| Pakdal Spring | Mountain, Benguet, Baguio | | | 110 | + | | | N | | | | N | 140 | T |
| Hot spring | Mountain, Mainit | large | | | | | 200 | | 93 | 0.7 | 750 | 210 | | 300 |
| Klondike Spring | Mountain, Benguet, Klondike. | large | | | + | | 40.9 | | 134 | T | 588 | N | 21.3 | 348.6 |
| Artesian well | Mountain, Tagudin | | | 100 | N | 786 | 20 | N | 8 | T | 400 | 70 | 40 | N |
| Do | Pangasinan, Dagupan (Calasiao Road). | 560 | Slightly brownish. | 245 | N | | | N | | | 29 | 128 (?) | 156 | 32 |
| Do | Pangasinan, Dagupan (market). | 220 | Slightly yellow | 290 | N | | | T-N | | | 67 | 193 (?) | 140 | 14 |
| Do | Pangasinan, Dagupan (river front). | | | 400 | 5 | 1,500 | 40 | 0.28 | 36 | 23 | 600 | N | 492 | 12 |
| Do | Rizal, Parañaque | | Nil | 270 | N | 1,070 | 74 | 0.44 | 30 | T | 340 | N | 330 | 50 |

[a] Iron and aluminum oxides ($Fe_2O_3+Al_2O_3$).

tically rainless months, and once during a period of frequent rains. The results of the two determinations, which are practically identical, indicate that deep-seated springs, such as Sibul Springs, may show surprisingly small seasonal variations in radioactivity. It should be pointed out that Sibul Springs shows a comparatively slight variation in flow throughout the year, so that the inference from the two isolated determinations just discussed is not considered to be at variance with the findings of other investigators. Thus Ramsey [19] found a greater emanation content in certain springs during periods of wet weather and great flow, and Steichen [20] observed an increase in activity in certain Bombay hot springs during the dry season, while the flow of water was considerably reduced. As pointed out by the latter writer, local conditions may well account for the differences noted.

For the sake of completeness we have noted in our data (Table I) all sources of water supply which are popularly considered to have special medicinal virtues. Either popular opinion is a poor guide to the medicinal value of a water, or else the medicinal properties of water are not to any great extent due to radium-emanation content. The waters with perhaps the greatest reputation, namely, Los Baños (12) and Sibul Springs (4 and 5), have relatively high radium-emanation contents, yet many others regarded as highly, such as Marilao (3), Pansol (9 and 10), Santo Tomas (36) and Klondike (72), contain little or no emanation. Moreover many waters high in activity, such as Batangas (1), Kiangan (66–71), Pagsanjan (19 and 21), and in general, the spring waters near Mount Banajao (13–17), are regarded with entire indifference.

Although emanation taken into the stomach is probably different in effect from that taken into the lungs, the following comparison may be of interest: Assuming that in ordinary respiration the average human being breathes 7 liters of air per minute, or 10.1 cubic meter per day, the emanation content thus brought in contact with the human system is $770 \times 10^{-12}$ curies, if the normal emanation content of the air in the Philippines [21] be taken as a basis for calculation. Therefore a person would have to drink about three-fourths liter of Sibul Springs water.

[19] Ramsey, R. R., The variation of the emanation content of certain springs, *Phil. Mag.* (1915), **30**, 815–818.

[20] Steichen, A., The variation of the radioactivity of the hot springs at Tuwa, ibid. (1916), **31**, 401–403.

[21] Wright, J. R., and Smith, O. F., loc. cit.

or one and one-half liters of Los Baños water, in order to take as much emanation into his system as he ordinarily secures by ordinary daily respiration alone.

## SUMMARY

The radioactivity of about ninety different Philippine waters, chiefly from springs and flowing wells, has been studied. The highest radium-emanation content encountered in a deep-well water was equivalent to $2100 \times 10^{-12}$ grams of radium; the highest in a spring water was equivalent to $1300 \times 10^{-12}$ grams of radium.

A test for the actual radium content of about twenty typical sources showed that the radioactivity encountered was due to emanation absorbed from materials with which the ground water had been in contact and was not due to dissolved radium salts. One sample of water showed a scarcely detectible trace of activity due to radium salts in solution; all the others tested gave negative results.

# ILLUSTRATIONS

**PLATE I**



TEXT FIGURES

Fig. 1. Field outfit for testing the radioactivity of waters.

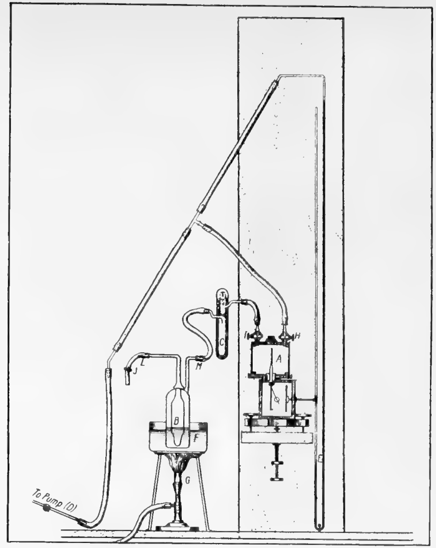


Fig. 2. Laboratory apparatus for testing the radioactivity of waters.

PLATE I.

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## SECTION A

## CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

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## THE PHYSIOLOGICAL ACTIVE CONSTITUENTS OF CERTAIN PHILIPPINE MEDICINAL PLANTS: II[1]

By HARVEY C. BRILL AND ALBERT H. WELLS

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila*)

FOUR PLATES

CONTENTS



### INTRODUCTION

An investigation of the physiologically active principles of the medicinal plants occurring in the Philippine Islands was begun by Bacon[2] in 1906. His investigation included *Alstonia scholaris* R. Br., *Datura fastuosa* Linn., *Caesalpinia sappan* Linn., *C. bonducella* Flem., *Entada scandens* Benth., *Tinospora crispa* Miers., *Argemone mexicana* Linn., *Erythoxylon burmanicum* Griff., *Aleurites moluccana* Willd., *A. trisperma* Blanco, and *Jatropha curcas* Linn.

It is recognized that many of the plants growing in the Archipelago that are reputed to be physiologically active have therapeutic value, but there is reason to believe that certain others possess no medicinal properties. Many of the plants found in the

[1] Receive for publication February, 1917. Botanical material and scientific and native names were furnished by Mr. E. D. Merrill and Dr. Leon Ma. Guerrero, of the section of botany, Bureau of Science; the historical data regarding local uses of the species investigated was supplied by Doctor Guerrero.

[2] Bacon, R. F., *This Journal* (1906), 1, 1007.

Philippines are not indigenous, but are found throughout the Malay Archipelago and India, while others are closely related to those occurring elsewhere. In India various species have been used both by European and native practitioners for medicinal purposes and are rated in their pharmacopœias as valuable drugs. This investigation of Philippine plants will show whether the same medicinal value is possessed by the species found here, will classify the active principles present, and will, where possible, furnish an accurate identification of the therapeutic body. No attempts will be made to furnish complete physiological tests of the active substances.

Individuals of related species or even plants of identical species may have different physiological constituents. Chernoff and others [3] state:

> It is possible that saponins from the same species of plants may differ, depending on the place where grown and the time of year when picked. We have some evidence of this point from work done recently on other species of plants.

The general methods used for the analysis of the plant materials are those of Dragendorff,[4] Kobert,[5] van Rijn,[6] Allen,[7] and other investigators who have worked on various medicinal plants. References to the latter are given in place.

In our investigations work has been based on material taken from fresh specimens collected and identified by the botanists of the Bureau of Science. In order to eliminate any possible loss due to decomposition, volatilization, and other factors during the drying period, work was done on both fresh and dried material. Quick drying of samples was obtained in a Freas oven at a temperature of 101° C. No appreciable changes were found in the analysis of the two differently prepared samples. Before extraction, the dried portion of the plant, supposed to contain the active principle, was ground to a fine powder. After maceration or percolation in the cold from eight to ten days the sample was usually extracted hot with the same solvent in order to assure complete extraction. Small samples of the plants

[3] Chernoff, L. H., Vichoever, A., and Johns, C. O., *Journ. Biol. Chem.* (1917), **28**, 438.

[4] Dragendorff, G., Plant Analysis. Baillière, Tindall and Cox, London (1884).

[5] Kobert, R., Beiträge zur Kenntnis der Saponinsubstanzen für Naturforscher, Ärzte, Medizinalbeamte. Ferdinand Enke, Stuttgart (1904).

[6] van Rijn, J. J. L., Die Glykoside. Gebrüder Borntraeger, Berlin (1900).

[7] Allen's Commercial Organic Analysis. Blakiston's Son & Co., Philadelphia (1913).

were always submitted to preliminary extractions for the purpose of determining the effect of the solvent.

Petroleum ether was used to remove any plant paraffin, wax, and oil; the extract was tested in the usual way for alkaloidal substances and, when thought necessary, for aromatic resins and essential and fixed oils. The residual dry plant matter was then extracted with ether, and this extract was tested in the usual manner for the presence of alkaloids and other principles; it was then allowed to evaporate, and the resinous mass was examined.

After the extractions with petroleum ether and ether, the plant residue was divided into several portions to be used separately for the determinations of alkaloids, glucosides, saponins, certain oils, albumens, and bitter principles.

### LOPHOPETALUM TOXICUM LOHER (CELASTRACEÆ)

*Abuab, batingui, dalinding* (T. in Rizal), *dayandag* (T. in Mindoro), *lanitan* (V. in Samar), *sudcad* (V. in Masbate), *puti-i-lalaque, puti-i-babae* (M. in Lanao), and *buyun* (M. in Zamboanga).[8]

*Lophopetalum toxicum,* of the Celastraceæ, is a tree well known among the mountain people of some parts of the Philippine Islands, due to the use they make of its bark to poison their arrows, spears, and other weapons.

According to the Remontados and Negritos of Rizal Province the poison is easily prepared. The method is as follows: The bark is removed, soaked, and bruised. The expressed juice is then evaporated to the consistency of an emulsion. In its preparation care should be taken not to let it come in contact with any sour substance in order not to diminish or neutralize its deadly action.

As an antidote against its poisonous effects the natives use a plant called *tamauyan* (*Strombosia philippinensis* Rolfe), or the fruits of *catmon* (*Dillenia philippinensis* Rolfe), or any other sour substance, like vinegar.

The fact that the properties of the compound are changed by warming with acids is proof of the glucosidal nature of the compound. The natives always concentrate the juice, as they believe it is harmless when in the dilute condition. The change taking place in the dilute juice is probably a hydrolysis to a harmless

[8] Throughout this paper T. stands for Tagalog; V. for Visayan; Il. for Ilocano; Sp. for Spanish; F. for Filipino; Pang. for Pangasinan; Pam. for Pampanga; N. for Negrito; M. for Moro; B. for Bicol; and Ifg. for Ifugao.

sapogenin by the action of various ferments. Heating destroys these, and as yeasts will not grow in the concentrated juice, there are no further changes after concentration.

Loher,[9] who was the first to find and describe *Lophopetalum*, at the end of his phytographic diagnosis writes the following:

> Cette espèce, voisine du *Lophopetaleum fimbriatum* Wall., habite les forêts de l'interieur de l'île de Luzon. Les Negritos, race indigène des îsles Philippines, recolectent l'ecorce très vénéneuse de cet arbre pour en préparer un extrait servant à empoissonner leurs flêches.

CHEMICAL EXAMINATION OF LOPHOPETALUM TOXICUM

The fresh bast fiber was quickly dried, pulverized, and macerated with petroleum ether for eight days. Slow evaporation of the petroleum ether leaves a mass of a yellow crystalline substance that is easily washed free from color by cold absolute alcohol. The white residue crystallizes in drusy clusters of acicular crystals. This crystalline mass is odorless and tasteless and has no physiological effect when administered in oil to a guinea pig. The yield is 0.8 per cent, the melting point is 183° C. It is fairly soluble in petroleum ether, ether, warm alcohol, and chloroform, but is insoluble in water. This white substance has the appearance of wax, responds to no tests for nitrogen, shows no acid or basic properties, and is slightly acted upon by alcoholic potash solution. The yellow coloring matter is easily taken up by animal charcoal. Ether extracts from the dry residue a small amount of yellowish resin of an acid nature. Washing out the petroleum ether and ether extracts with acidulated and alkaline water gave no traces of alkaloids present.

A water extraction of a portion of the plant residue after the above macerations froths greatly upon agitation and after hydrolysis reduces Fehling's solution.

The remaining plant material was submitted to the method of Kobert [10] for isolating saponins. The purified saponin substances were evaporated to dryness under reduced pressure, redissolved in 85 per cent alcohol, and allowed to stand several weeks in a vacuum desiccator. Irregular crystals separated out. A small amount of these was left after washing freely with 98 per cent alcohol. A solution of the crystals gives a precipitate with barium hydroxide and is easily hydrolyzed by strong acid. Mecke's reagent gives a purplish red coloration.

A guinea pig, weighing 523 grams, injected intraperitoneally with 0.0021 gram of these crystals, died in one hour and forty-five minutes. Symptoms of uneasiness began after three min-

[9] Loher, A., *Icones Boger* (1897), 1, 55. [10] Op. cit.

utes, followed by apparent blindness, increasing weakness of limbs, abdominal convulsions, exhaustion, and death. Similar injection into a guinea pig of 0.235 gram of the crude saponin substance, recovered from an extraction by methyl alcohol, gave the same symptoms, and death resulted after twenty minutes.

The sapogenin obtained by hydrolysis with emulsin formed groups of thick acicular crystals quite insoluble in water. The usual methods for detecting alkaloids failed to show the presence of alkaloids in the plant material. An extraction of the fresh bast fiber in sodium chloride solution gave no nitrogen substances precipitated by magnesium or sodium sulphate, thus indicating the absence of any of the common albumens of a toxic nature. As sapotoxins have slight value medicinally, no further examination was made of the compound.

This plant contains a physiologically active substance, a saponin which is poisonous in small quantities.

ERYTHROPHLOEUM DENSIFLORUM (ELM.) MERRILL (LEGUMINOSÆ)

*Malatabigui, calamantao* (T. in Tayabas), *malabunao* (B. in Camarines and Zamboanga), *n͠giricn͠gic, albihal* (N. in Cagayan), and *salsal* (Ibanag in Cagayan).

*Erythrophloeum densiflorum* Merr., of the Leguminosæ, is not considered poisonous among the Filipinos who make use of the wood for building purposes.

Lewin [11] says:

> Every species of *Erythrophloeum* is more or less rich in erythropleine, an alkaloid which is reputed to be a heart poison.

CHEMICAL EXAMINATION OF ERYTHROPHLOEUM DENSIFLORUM

*Erythrophloeum densiflorum* was primarily selected for analysis to determine whether or not it contained the alkaloid, erythrophleine, which is found in *Erythrophloeum guineense*. The routine method for alkaloids showed none present. The two methods [12] outlined by Gallois and Hardy were also closely followed. Neither method gave any indications of alkaloids, either amorphous or crystalline. In the Stas method the tartaric acid was found uncombined with any of the plant constituents. When treated with water, the concentrated alcoholic extract leaves a large quantity of red powder, probably decomposition products, such as phlobaphenes and dextrose resulting from the action of the dilute acid on the tannins. Neither the methyl alcohol nor

[11] Lewin, L., Traité de Toxicologie. Octave Doin, Paris (1903), 654.

[12] Gallois, N., and Hardy, E., *Journ. Pharm. et Chimie* (1876), 24, 26.

van Rijn's methods for isolating and testing saponins showed any positive results. No crystalline products of hydrolysis were obtained. Several injections of the aqueous solutions were made into guinea pigs, but without any results to indicate the presence of physiologically active constituents; also the water-insoluble portions were administered in oil without results. Tannins are present, but as they show an indifferent nature in regard to this work, their classification was not determined. From the water extracts they are entirely precipitated by lead acetate, while gold chloride gives a positive color in the Seyda test [13] for tannins.

The red substance insoluble in water and ether is fairly soluble in alcohol and in dilute ammonia, thus closely resembling the anhydrides of tannic acids or the phlobaphenes. The aqueous solution, from which this substance separates, strongly reduces Fehling's solution.

The bitter taste found in *Erythrophloeum densiflorum* may be attributed to the presence of the natural tannins. The important chemical difference between *Erythrophloeum guineense* and the Philippine species, *Erythrophloeum densiflorum*, is due to the presence of the alkaloidal substance erythophloeine in the bark of the former plant and its absence in the latter.

This result clearly shows that plants of the same morphologic characteristics may differ greatly, due to the nature of the substances that they elaborate in their economy.

### QUISQUALIS INDICA LINN. (COMBRETACEÆ)

*Piñones* (Sp. and F.), *niogniogan* (T. in Rizal, Bataan, Mindoro), *tan͠golo* (T. in Tayabas and Camarines), *talolon* (T. and V.), *talulong* (T. in Marinduque), *tan͠golong, tan͠gulong* (T. in Rizal and Manila), *tagarao* (T. in Rizal), *babebabe* (Pam. in Pampanga), *bo-nor* (V. in Mindoro), *balitadhan* (V.), *tal-lolang* (Il. in Camiguin Island), *tartaro* (Il. in Ilocos), *talulong* (Ibanag in Cagayan), *taun͠gon* (Butuan in Agusan), and *tartaraoc* (Zam. in Zambales).

The fruit of *Quisqualis indica,* called *niogniogan* or *piñones* in Manila, is a popular remedy. It is used in every country where it grows, and its anthelminthic properties are widely known.

Mercado,[14] writing in the last third of the seventeenth century, speaks of the anthelminthic properties of *piñones* seeds. Lou-

[13] Seyda, A., *Chem. Zeitg.* (1898), 22, 1085.

[14] Mercado, I., Libro de Medicinas de Esta Tierra, in Blanco, Flora de Filipinas. 3d ed. (1880), 4, 53.

reiro [15] considered that the seeds of *Quisqualis* had not only vermifugal properties, but also that it was a corroborant astringent and a nephritic.

Hanbury [16] speaks of this drug while referring to a work of Dr. E. J. Waring concerning the indigenous anthelminthics of India and remarks about its effectiveness against worms in children.

Soubeiran [17] says that the fruits of *Quisqualis* are an excellent vermifuge if four or five seeds are taken before breakfast on the morning of the first days of the month. Unsound fruits or those that have begun to open should not be taken, as they cause hiccough.

This symptom, which as a rule occurs only when too many of the seeds have been taken, does not occur in every individual. Some individuals can swallow great quantities of them without causing hiccough; for these it acts only as a laxative.

It is claimed that the roots also possess the same vermifugal qualities as the kernel.

### CHEMICAL EXAMINATION OF QUISQUALIS INDICA

The leaves, roots, and fruit of *Quisqualis indica* were analyzed. We found no compounds in the leaves or roots which would seem to have any physiological effect. No alkaloid was found. None of the extracts showed any results with dogs or guinea pigs when administered intraperitoneally or by the mouth.

The yellowish kernels from six of the dry fruits were eaten by an adult. They produced the effect of a mild laxative. The nuts contained 12.96 per cent moisture and a yellow oil, representing 28.37 per cent of the original nut.

TABLE I.—*Constants of the oil extracted from the dried meat of the nut of Quisqualis indica (ether extraction).*

| | |
|---|---|
| Specific gravity at 30° C. | 0.9075 |
| Refractive index at 30° C. | 1.4585 |
| Polarization | 0.00 |
| Saponification No. | 187.97 |
| Iodine No. (Hanus) | 66.49 |
| Reichert Meissl. No. | 1.4 |
| Acetyl value | 3.787 |
| Appearance | clear, yellow |

[15] Loureiro, J. Flora Cochinchinensis. Ulyssipone (1790), 1, 274.

[16] Hanbury, Daniel, Notes on Chinese Materia Medica. John E. Taylor, London (1862), 15. Reprinted from *Pharm. Journ.* for May, July, October (1861).

[17] Soubeiran, L. Léon, La Matière Médical chez les Chinois. G. Masson, Paris (1874), 262.

A slight separation of the less liquid components is observed when the oil has stood for several months. Ten cubic centimeters of the oil produced purging in an adult person without the hiccoughing, which is produced by taking a number of the whole kernels. The oil failed to show anthelminthic properties when given to children.

An alcoholic extract of the residue, after petroleum ether and ether extractions, gives by vacuum evaporation a fragrant, pleasant-tasting substance readily soluble in water and precipitated from alcoholic solution by ether. When dry, it is white and vitreous. It strongly reduces Fehling's solution. It is probably a sugar. The yield is about 1.5 per cent. No apparent physiological action is noticed from the administration of it to adult persons or to guinea pigs. The original plant kernel after the above extraction was macerated with water. Much mucilaginous substance was obtained. This substance swells in water, forming a translucent solution. It is precipitated in a flocculent white state by alcohol. Boiled with dilute hydrochloric acid, it is converted into reducing sugars. The substance is believed to be vegetable mucilage or a gum, which is fairly soluble in water. A solution of this gum forms precipitates with most of the group reagents for alkaloids. It may possibly be due to this fact that some investigators report the presence of alkaloids in *Quisqualis indica.*[18]

After the removal of the gums from solution and evaporating and cooling of the filtrate, crystals of potassium sulphate formed, giving a yield of 3.87 per cent of purified compound. It may be that these two latter products are accountable for the medicinal properties attributed to the plant. It was not thought advisable with the small amount of material at hand (it being the end of the bearing season for sound fruit) to attempt to perform physiological tests of a conclusive nature.

An oil was extracted from the seeds that has purgative properties, a physiologically inactive substance resembling a sugar was isolated by alcohol extraction, a gum which gave many of the reactions of an alkaloid was extracted from the seeds by water, and 3.87 per cent of potassium sulphate were found.

### TYLOPHORA BREVIPES (TURCZ.) F.-VILL. (ASCLEPIDACEÆ)

*Saruncad, sarungcar* (Il. in Zambales), *pasuca* (T. in Zambales), *sayoncal* and *dail* (Pang. in Pangasinan).

[18] Hartwich, Carl, Neue Arzneidrogen. Julius Springer, Berlin (1897), 282.

*Tylophora brevipes* has been found in Zambales, Pangasinan, and Cagayan Provinces, Luzon, and also in Mindoro. So far as we know, nothing has been written about this drug, which is much valued among the Filipinos of the northern provinces of Luzon. The Filipinos use only the fresh or dried roots in the form of a decoction without regard to dose or strength. It is prescribed in cases where a powerful and quick emetic is required. Herb doctors give it as a remedy against fevers, indigestion, incipient tuberculosis, asthma, and cough, to help the ejection of bronchial mucus. Some herbists use it as an emmenagogue and even as a cure for gastralgia. It is said that if a patient is given a very strong dose it may produce vomiting, which will finally kill the patient.

*Tylophora asthmatica* W. & A., a species very closely resembling *T. brevipes,* has considerable reputation in India for its medicinal qualities. Kirkpatrick is quoted as saying of his experience with *Tylophora asthmatica:*[19]

> I have administered this medicine in at least a thousand cases and found it most valuable. In dysentery, and as a simple emetic, it is in every way comparable with Ipecacuanha. The dose is from 20 to 30 grains, with half a grain or a grain of Tartar Emetic, if strong emesis is required. If the dysentery distinctly arises from intermittent disease, Quinine is conjoined. The form of the medicine I use is the powder of the dry leaf. If the root were used, the supply would soon be exhausted; besides I have found it less certain than the leaf. The preparation of the juice would at all times be troublesome and tedious. In catarrhal and chronic coughs it seems to act well. Its efficacy as a substitute for Ipecacuanha, not only as a simple emetic but as a remedy in dysentery, asthma, and catarrhal affections, is confirmed by the report of Dr. Oswald, Mr. Moodeen Sheriff, and others. According to the latter, the best treatment of snake bites consists in producing free emesis by the expressed juice of this plant, and following up its use with diffusible stimulants.

Dymock[20] likewise speaks in glowing terms of its virtues. Waring[21] refers to it as country ipecacuanha. Because of the flattering accounts of the results arising from the use of *Tylophora asthmatica* and the reputation that *T. brevipes* already enjoys among the Filipinos, it was decided to make a chemical examination of the latter to determine if its physiological activity

[19] Waring, E. J., Pharmacopœia of India. W. H. Allen and Co., London (1868), 458.

[20] Dymock, W., The Vegetable Materia Medica of Western India. Education Society's Press, Byculla, Bombay. Trubner & Co., London. 2d ed. (1885), 519.

[21] Waring, E. J., Bazaar Medicines. J. & A. Churchill, London. 4th ed. (1883), 152.

was due to the presence of a compound similar to the alkaloid found in *T. asthmatica.*

CHEMICAL EXAMINATION OF TYLOPHORA BREVIPES

Specimens of the fresh leaves and roots were used for the analyses.

A petroleum ether exhaustion of the dried roots gave a slight amount of volatile aromatic oil and no traces of alkaloids. When separated from the wax and other extracted matter by steam distillation, the yield of yellow oil was slightly over 0.10 per cent. The residual plant materials were extracted with a chloroform-alcohol mixture. The coloring matter and resinous substances were precipitated with the chloroform on the dilution of the mixture with water acidulated with hydrochloric acid, while the separated alcoholic solution was concentrated to a syrup, again extracted with alcohol, then concentrated, and this concentrate extracted with water. The final orange-colored aqueous solution reacted positively for alkaloids. Two cubic centimeters of this solution given intraperitoneally to a guinea pig of 420 grams' weight caused death within two and one-half hours. Vacuum evaporation and purification through alcohol gives a small yield of the alkaloid in the form of acicular crystals often grouped and radiating (Plate I, fig. 1). Administered to guinea pigs, 0.10 gram of the colorless crystals produced spasms and symptoms of vomiting. An acid water extract of part of the original ground plant material clarified by the neutral lead acetate method and concentrated gave identical crystals from an alcoholic extraction of the concentrate. Concentrated sulphuric acid gives a red color, while nitric acid gives a magenta red color with this compound. The crystals have a peculiar, somewhat acrid [22] and bitter taste and are soluble in water and in alcohol. The quantity separated was insufficient for quantitative chemical analysis.

In 1890 Hooper, working on *Tylophora asthmatica,* isolated an alkaloid which he termed "tylophorine." The presence of such a compound in the Asclepiadaceæ has been noticed by several investigators, notably by Broughton,[23] of Ootacamund, in 1872, when he obtained a small quantity of crystals insufficient for analysis. Extracts from the leaves of *Tylophora brevipes* contain an alkaloid reacting like that found in the bark.

The work done by us on *Tylophora brevipes* shows the presence

[22] Flückiger, F. A., and Hanbury, D., Pharmacographia. A History of the Principal Drugs of Vegetable Origin. Macmillan & Co., London. 2d. ed. (1879), 427.

[23] Flückiger and Hanbury, loc. cit.

of an alkaloid which is similar in action to tylophorine, found by Hooper [24] in *Tylophora asthmatica* W. & A. and recognized in the dispensatory.[25]

The local plant can be used in the same manner as *T. asthmatica,* since its action is due to the presence of an alkaloid identical with or closely resembling tylophorine.

TODDALIA ASIATICA (L.) KURZ (RUTACEÆ)

*Dauag, dauag manóc, cayutanang baguing* (T. in Rizal), *atangen* and *bugkan* (Ifg. in Benguet).

This plant is found in many places of the Philippine Islands, being a species of wide geographic distribution.

Notwithstanding the fact that the root of this plant has been widely known for several centuries for its febrifugal and antidiarrhœal properties, even to the extent of having been added to some of the European pharmacopœias under the name of *Radix indica lopeziana,* or "root of Juan Lopez Pigneiro," Filipinos know nothing of its medicinal properties.

Dymock,[26] says:

> This scandent shrub appears to have been one of the plants known to Sanskrit writers as kánchana or golden, on account of the orange color of its fruit.

Yet, in his compilation of the Sanskrit books about medicine, Udoy Chand Dutt says nothing about this drug, although its use is apparently general in India.

Flückiger and Hanbury [27] say that the root of *Toddalia* was first known in 1671, thanks to Doctor Redi, an Italian, who described it from the samples in his possession gathered by Juan Lopez Pigneiro near the mouth of Zambesi River, East Africa. In 1771 this drug was introduced into European medicine by Gaubius as a remedy against diarrhœa. Its reputation became so great that in 1792 it was included in the Pharmacopœia of Edinburg, although its botanical origin was not noted. As often happens with vegetable drugs without any specific action, *Radix indica lopeziana* has fallen into disuse.

The chemical composition of *Toddalia* root is not yet clear, notwithstanding the analytical researches done by Flückiger and Hanbury and also by Dymock. The former say that they were

[24] Hooper, David, *Pharm. Journ. & Trans.* (1891), 21, 617.

[25] Hare, Caspari, Rushy, National Standard Dispensatory. Lea & Febiger, Philadelphia (1908), 269.

[26] Dymock, W., Pharmacographia Indica. Kegan Paul, Trench, Trübner & Co., Ltd., London (1893), 1, 260.

[27] Op. cit., 777.

unable to prove the presence of berberine [28] in the drug, and the latter studied only the volatile oil obtained by the distillation of the leaves. Nadkarni [29] is of the opinion that the root contains berberine.

In view of this difference of opinion George Watt, author of the Dictionary of the Economic Products of India, bewails the fact that none of the Hindu chemists has endeavored to find out the composition of the fresh material.

Some laboratory work has been undertaken by us with the object in view of determining whether the intensely bitter taste of the root of *Toddalia asiatica* is due to berberine, to some bitter principle, or to an alkaloid of an unknown nature.

Following is the special opinion of Moodeen Sheriff regarding the virtues of *Toddalia asiatica,* as it is given in Watt's dictionary:

> I have been using the root-bark in my practice for the last sixteen or seventeen years, and do not hesitate to say that it is, as an antiperiodic and antipyretic, equal if not superior to quinine and other alkaloids of Cinchona and to Warburg's tincture respectively. As a diaphoretic, it is decidedly superior to Pulv. Jacobi Vera, and as a tonic to Gnetian and Calumba. It is highly useful in effecting a cure in all idiopathic and uncomplicated fevers, whether periodical or continued. It is best used in tincture and decoction and I make these preparations three or four times stronger than those generally in use. This is the chief reason, I think, which has rendered the drug so successful in my hands. The analogy between the medicinal properties of the root-bark of *T. aculeata* and those of the root of *Berberis aristata* and a few other species of *Berberis* is very great and complete, there being no difference whatever. Therefore, everything I have said about the preparations, doses, therapeutic used and the manner of using the tincture and decoction of the latter is quite applicable to those of the former. The drug under consideration, however, has one great advantage over the root of *Berberis aristata* and other species of *Berberis,* namely, that it is procurable in every large bazár of Southern India; whereas the roots of the latter plants must be procured from distant places, such as the Nilghiris, Shevaroy Hills, Central and Northern India, etc.,

The following formulas belong to the Pharmacopœia of India (1868):

> Tincture of Toddalia (Tinctura Toddalia). Take of the root-bark of Toddalia, bruised, two ounces and a half; Proof Spirit, one pint. Macerate for seven days in a closed vessel, with occasional agitation; strain, press, filter, and add sufficient proof spirit to make one pint. It may also be prepared in the same manner as Tincture of Calumba.
>
> Dose: From one to two fluid ounces twice or thrice daily.

[28] Op. cit.

[29] Nadkarni, K. M., Indian Plants & Drugs with their Medical Properties and Uses. Norton and Co., Madras (1910), 398.

Infusion of Toddalia (Infusum Toddalia). Take of the root-bark of Toddalia, in coarse powder one ounce; boiling water, ten fluid ounces. Infuse in a covered vessel for one hour, and strain.

Dose: From one to two fluid ounces twice or thrice daily.

CHEMICAL EXAMINATION OF TODDALIA ASIATICA

The brittle root bark cleared of the outer layer was finely ground, dried at a low temperature, and exhausted in the usual way with petroleum ether, ether, alcohol, and water.

Petroleum ether removed a small quantity of wax and a little resin, which was dissolved in a sharp-tasting pungent oil. It is possibly due to the not unpleasant taste of this oil that parts of the plant are used in India as a condiment. The resin is easily crystallized from an ether-alcohol mixture in groups of elongated prisms or needles.

An absolute alcoholic extraction of the dried plant residue gives a yellow solution which, when purified by repeated evaporations and alternate extractions with water and alcohol, yields a final aqueous solution of a greenish yellow color, giving the group reactions of alkaloids. A few of the reactions are as follows:

Gold chloride, yellowish precipitate; platinic chloride, no precipitate; Mayer's solution, white precipitate; phosphomolybdic acid, white precipitate; potassium cadmium iodide, white precipitate; mercuric chloride, white precipitate (light); potassium mercuric iodide, white precipitate; Kraut's reagent, ochraceous orange precipitate; picric acid, yellow precipitate; bromine, orange precipitate (heavy) (darkens). Vacuum evaporation leaves a thick amorphous alkaloid. A portion diluted with alcohol, spread in thin sheets and allowed to evaporate slowly, formed crystals (Plate I, fig. 2). Both the hydrochloride and sulphate were made, and a small quantity of crystals of each was obtained. The free alkaloid both in the amorphous and crystalline condition is soluble in the cold in distilled water, giving a bright yellow color, and is fairly soluble in methyl alcohol and ethyl alcohol, slightly soluble in acetone, chloroform, and ethyl acetate, while only slight traces dissolve in ether, petroleum ether, benzene, and amyl alcohol. From this may be understood the property which it possesses of not being easily separated from either alkaline or acid solutions by agitation with immiscible solvents.

The alkaloid has a persistently bitter taste, but is not as intensely bitter as the alkaloid found in *Lunasia amara* Blanco. The crystalline forms of the free alkaloid and of its salts seem identical with those of berberine, with which comparative tests

were made. The alkaloid conforms to all the tests given by Mulliken [30] for berberine. Like berberine the salts have an intensely yellow color and an extremely bitter taste. A solution of iodine in potassium iodide gives a brown precipitate of $B.HI.I_2$, crystallizing from hot alcohol, in long adamantine needles, which are insoluble in water and cold alcohol. Warming with concentrated sulphuric acid gives an olive green color. A fragment of $NaNO_3$, stirred into the solution in $H_2SO_4$, gives a violet streak. Chlorine water gives the characteristic purple zone effect. By the careful addition of weak nitric acid acicular crystals of the yellow nitrate are formed (Plate II, figs. 1 and 2). The salts are decomposed by heat. These reactions are characteristic of berberine and of the alkaloid from *Toddalia asiatica.* Since the alkaloid responds to all the characteristic reactions for berberine, we feel justified in concluding that *Toddalia asiatica* Kurz of the Philippine Islands contains berberine.

### LUNASIA AMARA BLANCO (RUTACEÆ)

*Lunas* (T. in Rizal, Bataan, Bulacan, Mindoro, and Pampanga), *paitan, pait, lunas bondoc* (T. in Bataan), *malasanqui, lunas na putí* (T. in Rizal), *bayabayabasan, saltiqui, santiqui* (T. in Laguna), *abdong cahoy* (T. in Batangas and Laguna), *malaligás na babae* (T. in Baler), *malacacao, cacaocaocaoan* (T. in Batangas), *lubilubi* (V. in Cebu), *labao* (V. in Ticao Island), *paetan* (V. in Leyte and other southern Islands), *pait-pait* (V. in Zamboanga), and *saguit* (M. in Zamboanga).

*Lunasia amara* is a species widely scattered throughout the Archipelago; it is found in most provinces and islands.

The literature of *Lunasia* is scant, for up to the time when Dr. W. G. Boorsma [31] began his investigations with authentic material of this species all that had been published with reference to its chemical composition was in reality about the bark of *abuab* (*Lophopetalum toxicum* Loher), which is utilized by some of the inhabitants of the Philippines to poison their weapons.

This unfortunate confusion arose from the fact that *Lophopetalum toxicum* had been sent to European museums by Dr. Schadenberg, a resident of Manila at the time, with the erroneous name of *Rabelaisia* (*Lunasia*). Plugge, and other investigators, who could only avail themselves of the material received at the museums, were victims of this error.

[30] Mulliken, S. P., The Identification of Pure Organic Compounds. John Wiley & Sons, London (1916), 2, 261.

[31] Boorsma, W. G., *Bull. Inst. Bot. Buitenzorg* (1900) **6**, 15.

Thus rebelaisine, of Plugge, should be therefore called lophopetaline, a substance utterly different from lunasin, which was obtained by Lewin and later identified with that obtained by Boorsma from *Lunasia costulata* Miq. (=*L. amara* Blanco). This author, in his commentary on the results of his research, says that he obtained an amorphous alkaloid, hygroscopic, of bitter taste and nonvolatile, from the bark of *Lunasia costulata*. Lunasin was dark grayish and was very soluble in water. Eight milligrams in a hypodermic injection acted as a cardiac poison and killed a frog of 78 grams' weight; the heart stopped in systole. A dose of 20 milligrams injected into a guinea pig produced a severe intoxication with complete paralysis for some time, though without occasioning death. Lunasin has been also found in the hard wood of the tree.

Father Juan J. Delgado [32] mentions three species of paetan—the first and second identified by Fernandez-Villar as *Lunasia amara* Blanco. There are several distinct species of *Lunasia* found in the Philippines, so that perhaps Delgado's statements really refer to more than one form.

Following is a translation of a part of what Delgado writes concerning lunas or paetan.

> Paetan is a name common to three species, all of them very bitter, from which it derives its name, which we might translate as "bitterness itself." This is true of the one that is larger than the rest, whose branches grow to be of the size of the wrist. I wished to make experiments on this one, and for that purpose had some brought from Panamao Island. It is very bitter and acts as a poison. By merely chewing a very small bit of its bark, I was hardly able that day to remove the bitterness from the tongue, experiencing some sort of convulsions for three days. I was obliged to take some antidotes and cold water baths, but after the three days were over, I felt exceedingly robust and well.
>
> All this leads me to believe that if this plant were carefully studied, its value as a medicine would be learned. A lad who tasted it at the same time I did immediately felt the same effects, but having in his case provoked nausea, was soon well. Some of the natives use an infusion of the bark of paetan to cure eye trouble; the solution is so strong that the bitter taste becomes evident in the throat and mouth.
>
> The second paetan is a smaller tree, which is found in the smaller islands of the Archipelago, and is very well known and much valued for its medicinal fruits. It is an antidote for all poisons whether they be from witch-craft or from snakes, or poisonous animals or fish. Half a real in powdered form will cure a severe stomach ache due to any cause; it is admirable for infected wounds, for it will clean and cure them in a short time. Finally it is one the antidotes used to make the "óleo de japlas."

[32] Delgado, J. J., Historia general sacro-profana, politica y natural de las islas del Poniente llamadas Filipinas (1892), 611.

I honestly believe that it would be a fine remedy for sciatica and gout; those who suffer from these diseases may try without any fear.

From the above it appears that instead of being a harmless drug lunasine should have very strong properties. Attention is called to the fact that the author does not mention the use which, according to some, the Filipinos made of it to poison arrows. This statement, so often made by the foregoing writers, is perhaps a misinterpretation of Blanco's statement in the original description of the species. A translation of his remarks regarding the use of the wood follows:

The grain is very fine and close, and the wood is so hard that the Negritos use it instead of iron for the points of their arrows.

We are almost convinced of this misinterpretation, for notwithstanding our careful investigations we have not been able to find a Filipino who could corroborate the assertion made by those who have written about *Lunasia* being used to poison arrows.

The investigation of medicinal and poisonous plants which the Bureau of Science is carrying on at the present time has no further available information in regard to the immediate medicinal uses of the species here in question than that obtained from Laguna Province, which translated is as follows:

The juice of either the dried or fresh seeds, macerated in alcohol or cooked in oil and then concentrated, is generally used against the bite of poisonous animals.

It is the general opinion among herb doctors that not only the bark, but also the seeds are a good remedy to cure gastralgia in general and certain adynamic conditions of the digestive organ.

## CHEMICAL EXAMINATION OF LUNASIA AMARA

The bark and leaves were used for analysis.

From the prepared bark, petroleum ether extracts a small quantity of vegetable wax and traces of alkaloids; ether extracts contain no traces of alkaloids, but a small quantity of wax, not removed by the petroleum ether, and the chlorophyll existing in the bark. Following the ether extraction a mixture of equal parts of ethyl and methyl alcohols removes a considerable quantity of alkaloidal substance.

Purification by repeated alternate extractions with water and alcohol leaves the alkaloid in an amorphous condition. The yield is about 0.6 per cent. It is extremely bitter, has a brownish color, and is yellow in alcoholic solution. It is readily soluble in water and takes up water when exposed to the air. It is

soluble in hot absolute ethyl and methyl alcohol, from which solutions by careful evaporation crystals were obtained (Plate III).

The amorphous compound is but slightly soluble at 20°C. in ethyl and methyl alcohol. It is almost insoluble in cold chloroform, ethyl acetate, and petroleum ether and is insoluble in cold ether, benzol, amyl alcohol, and acetone. The amorphous substance precipitated from the ethyl-methyl alcoholic solution by ether is very hygroscopic, quickly changing from a white solid to a reddish brown aqueous solution. Plate III, fig. 1, shows the dendritic crystals which formed quickly from absolute alcohol. Plate III, fig. 2, shows cubical crystals formed from the amorphous substance on long standing in a vacuum desiccator over calcium chloride. Both forms of crystals were soluble in the organic solvents that dissolve the amorphous alkaloid and were toxic in large dosage in their action toward guinea pigs.

The hydrochloride, nitrate, and sulphate were made. The hydrochloride crystallizes with difficulty in acicular form from a weakly acid solution (Plate IV, fig. 1).

Besides the above colorless crystals a few prisms may be observed present in the microphotograph. Both forms of crystals react positively for alkaloids. This suggests possibly the presence of two alkaloids.

The nitrate forms in pale yellow elongated prisms, and the sulphate forms in plates or prisms of the same color. An aqueous solution of the purified free alkaloid reacts heavily with the general group reagents:

Iron chloride gives a reddish solution; gold chloride, a yellow precipitate; platinic chloride, a pale yellow precipitate; bromine, a yellow precipitate; potassium-cadmium-iodide, a white precipitate; mercuric chloride, a white precipitate; potassium iodide, a white precipitate (slight); picric acid, a yellow precipitate; Mayer's reagent, a white precipitate; Kraut's reagent, a red precipitate.

The compound was tested for nitrogen; it reacted positively. The bromine compound is unstable, easily decomposing when filtered free of excess bromine. A portion of the crude alkaloid was purified by precipitation with Kraut's reagent and broken up by alkaline carbonate. The pure alkaloid obtained was not a large yield and was amorphous.

The dried, finely ground leaves were exhausted in the usual manner with petroleum ether, ether, and chloroform-alcohol mixture. The petroleum ether solution contained a neutral wax and a small quantity of an essential oil of yellow color and sharp

taste and no traces of alkaloids. The ether solution gave a small quantity of aromatic acid resin and traces of the same essential oil. After dilution and precipitation of the coloring matter with the chloroform, the aqueous solution was evaporated on the steam bath, and the product was purified according to the method previously used. The same alkaloid was found to be present in the leaves, but seemingly in lesser quantity than in the bark.

In both cases the exhausted plant material was finally macerated with hot water. The water extract showed but little of the alkaloid not extracted by the organic solvents. Neither acid nor alkaline extractions of the original plant material were made for the reason that evaporation of such solutions prepared from the isolated alkaloid showed a marked decomposition on heating. Solutions of the free alkaloid as prepared from approximately neutral solution could be evaporated to dryness without vacuum and without any apparent decomposition. The salts were readily decomposed by warming on the steam bath.

Two cubic centimeters of a 10 per cent solution of the free alkaloid produced apparent, great weakness when injected into a guinea pig. The animal recovered. About 0.8 gram given to a dog produced apparent weakness, a desire to sleep, and a slowing of the heart action. There were no signs of pain. The animal recovered its normal activities after two hours had elapsed.

*Lunasia amara* contains an alkaloid or possibly two alkaloids that have some physiological activity.

### ROUREA ERECTA (BLANCO) MERRILL (CONNARACEÆ)

*Palo santo* (Sp.-F. in Rizal), *camagsang baguing* (T. in Rizal), *lenamo* (Cuyo Island), *malagranada* (F. in Bulacan), and *gangó* (Il. in Ilocos Norte).

The name camagsang baguing is better applied to *Rourea volubilis* (Blanco) Merrill.

The family Connaraceæ, to which this plant belongs, yields few drug-producing plants. With the exception of two species of *Agelaea,* two of *Connarus,* one of *Cnestis,* and another of *Rourea,* all are employed in popular medicine wherever they grow, though none go beyond the limits of quackery. The family is of slight importance in materia medica. The seeds of *Rourea* are poisonous.

It may be generally stated that the Connaraceæ are characterized by the presence in their tissues of astringent elements and balsamic resins. Judging from the uses indicated by Fili-

pinos, the roots of *Rourea erecta* are more astringent than balsamic.

The data gathered up to date in regard to the use of palo santo in the Philippine Islands are to a certain extent contradictory. Some say that a decoction from the roots up to the dose of a teaspoonful is an emetic, but if this dose is exceeded, it is a poison. This decoction mixed with the food and given to hogs and dogs will kill them. The animal becomes nauseated and dies, but if nausea does not follow, the animal will swoon and will expire without recovering.

Information received from La Union Province presents similar evidence with some details of the symptoms as follows:

> The animal staggers and falls to the ground moaning and expires after a while.

Others claim that death does not follow immediately, but after an interval of three or four days.

Other information received from Samal (Bataan) is that the decoction from the bark of the roots expedites childbirth and that the fruits are poisonous and are used to kill dogs.

And lastly, reports from Pangasinan do not mention the roots or the stems, but state that the fresh or dried leaves in decoction are used to cure gastralgia and are an absorbent.

The medicinal properties which Delgado [33] attributes to palo santo (*guicos guicos, hanmabao*), and according to Blanco also known as *camagsá taquilis* (Tag.), *ungali na mapulá magtabig,* and *mavindato* (Visayan and Pampango), are those that cause the natives from the vicinity of Manila to make use of the roots of the species herein mentioned. However, guicos guicos is not *Rourea erecta* (Blanco) Merrill, but *R. volubilis* (Blanco) Merrill, which was identified by Fernandez-Villar as *Rourea heterophylla* Planchon, a synonym of *R. volubilis* Merr.

Delgado states that one of the medicinal vines for many ailments is that which is called by the natives of some islands guicos guicos, while in others they call it hanmabao. The Spaniards call it palo santo, due to its admirable properties. It is a fine remedy for lockjaw and colds, which are common maladies in this country. The decoction of this vine is very good for those who suffer from venereal diseases, and has sudorific properties.

De Mercado, in his Libro de Medicinas de esta Tierra, and Blanco, in his Flora de Filipinas, also speak of palo santo, which

[33] Delgado, J. J., Historia general sacro-profana, politica y natural de las islas del Poniente llamadas Filipinas (1892), 780.

is called by the former *camunin* or *guayacan,* as a sudorific and purgative.

Having in mind the opinion of these three authors about guicos guicos and the scant information about camagsá, which is more commonly known as palo santo, it is easily understood how the Filipinos of to-day have mistaken the two species—confusing *R. erecta* and *R. volubilis* and making use of the former instead of the latter. It is possible that the three observers were misinformed about the botanical origin of the medicinal species or it is possible that both plants have the same properties, though the latter supposition seems untenable.

### CHEMICAL EXAMINATION OF ROUREA ERECTA

The roots and fruit are the parts used.

Extractions from the roots show a high percentage of plant wax, no alkaloids, glucosidal bodies, or any active principles. After the extraction with ether, extraction with ethyl alcohol (92 per cent) gave a thick mass that amounted to 24 per cent of the original plants when evaporated under 600 millimeters vacuum. This mass consisted of tannin substances, not alkaloidal in character (phlobaphene), and other coloring matter. The coloring matter is a bright magenta. It is red in acid solution and gives a dark green precipitate in alkaline solution. The red color is soluble in water and easily washed free from the other solid extracted matter. It is also easily decomposed by concentrated hydrochloric acid.

Water extractions of the roots gave no decided symptoms when administered to a dog or injected into a guinea pig.

The berries were analyzed both in the fresh and dried state. The toxicity of the ground, fresh berries was not greater than that of old specimens. In fact, the highest toxic effect was obtained from a residual worm-eaten specimen that had had all opportunity to ferment and undergo decomposition. Kobert [34] has made the statement that the active principle of *Rourea oblongifolia* is destroyed when the plant dries. This is not true in the case of *R. erecta.* Experiments were made on healthy dogs using the ground berries and the numerous products of extraction. Taking the freshly picked, finely ground berry and administering it in meat to a dog, no effect was noticeable until the third day, when slight weakness was apparent. These symptoms were manifested after the consumption of 20 grams of the berry in a period of seventy-two hours. Only slight, increasing

[34] Kobert, R., *Centralbl. f. klin. Med.* (1893), 14, 930.

weakness was noticeable up to the sixth day. During the following thirty-six hours the dog lost control of voluntary movement, and the activity of the salivary glands seemed greatly increased, a large volume of clear liquid passing from the mouth. The pupils were dilated, but vision seemed good. There were no convulsions before death. The dried fruit gave similar results when administered in much smaller dosage. Five grams of dry, worm-eaten seeds were finely ground and given to a healthy dog of full growth. Death followed after a period of thirty-eight hours. An examination showed no abnormal conditions. There was no congestion, the bladder was empty, and the liver, spleen, kidneys, and lungs were normal. The heart was full. Renson [35] states that carnivorous animals are affected by eating the berries, while birds and fowls consume it with impunity.

The dried seeds, finely ground and extracted with petroleum ether, gave a white crystalline mass containing a small amount of ether-soluble resin of a yellow color. Attempts were made to oxidize this white product from the berries (melting point 64° C.) by heating with potassium permanganate in sodium carbonate solution for two hours on a steam bath; the manganese oxides decomposed by sulphurous acid, and the resulting product recovered. The compound had the melting point of the original body (64° C.). No oxidation took place under these conditions.

The compound was treated with ammonium hydroxide in 50 per cent alcohol solution and sodium carbonate in excess on the water bath for two hours; hydrochloric acid was added, and the mixture was filtered. The product melted at 64° C., the same as the original sample. Also the original compound was treated in acetic acid with bromine, by heating on the steam bath for one and one-half hours. When the solution cooled, a flocculent precipitate resulted. This precipitate, washed free of acetic acid and bromine, gave a melting point of 63° C.; the orignial compound was recovered. The compound showed no physiological effect, and it was concluded to be plant wax. The plant residue left after the extraction by petroleum ether was extracted with cold and hot absolute alcohol. No toxic substances were found in this solution. Precipitation was obtained from the alcohol extract by dilutions with water. An aliquot part of this precipitate was vacuum dried and extracted by solvent. The products were administered in large dosage to dogs without resulting effect. Extracts were obtained from this same plant material using consecutively the solvents ether, chloroform, amyl alcohol,

[35] Renson, Carlos, *Pharm. Journ. & Trans.* (1891–92), 22, 982.

and ethyl acetate. When thought necessary, these extractions were on material made acid or alkaline. The extracts freed from the solvent produced no physiological effects on dogs or guinea pigs. In no case was any disturbance in the activity of guinea pigs observed from the administration of any portion of this plant. These results confirm Renson's conclusions regarding the nonpoisonous character of the plant toward the Herbivora.

After the extractions with organic solvents neutral warm water was used to extract the plant. Vacuum evaporation of the filtered solution gave a small mass of crystalline substance which was recrystallized once from methyl alcohol followed by ethyl alcohol. The quantity was insufficient for analytical purposes. Eight milligrams were given a healthy 1-year-old dog. The compound exhibited the same effect as that produced by the crude drug. In this case the animal showed a change in mental condition similar to that observed by Renson [36] in his "second form of poisoning." Although the plant material *congoura* (*Rourea oblongifolia*) used by Renson is not the same as that used by us, yet our results indicate that these plants contain the same active principle. He describes what he terms the "second form of poisoning" in the above reference as follows:

*First or Acute Form of Poisoning, followed by Death.*

Two or three hours after the hypodermic injection the animal commences to vomit without great effort, it expels fecal matters, and trembles a little. An increase of activity in the salivary glands is than observed, a clear and limpid liquid trickling from the mouth, drop by drop and in quantity relatively great, as though jaborandi had been taken. Soon the movements in walking become uncertain, the animal stumbles, and appears intoxicated. Later it remains lying down and there is a loss of voluntary movements. At last convulsions occur, the mouth remains open, and the pupils are dilated. These convulsions are accompanied by moans and blinking of the eyelids. Then appears a most curious phenomenon. The dog, although lying on its side, executes the movements of walking. With ears and tail erect, it shakes its head in an almost lively manner, and there is no doubt it believes it walks. This dream, if I may so call it, immediately follows the convulsive attack. The attacks are repeated a great number of times, and in the intervals there are hiccups and sudden starts. At last the animal, completely worn out, falls into a comatose state, its respiration becomes unequal, it emits a little blood by the nostrils (in certain cases, but not in others), and dies at the end of ten to twelve hours.

*Second Form of Poisoning, followed by Recovery.*

It suffices to introduce half a cubic centimeter of the liquid extract of Cangoura into the organism, either by means of the skin or the stomach, to produce the following effects in a dog of average size. The day of injection

[36] Loc. cit.

and the following day the animal appears perfectly well. Two days afterwards the cerebral disturbances appear. Suddenly, without apparent cause, it rushes about in an unbridled career, barking loudly, and seeming to pursue an imaginary prey. After that it stops, with its tail between its legs, and begins to howl in a very disagreeable fashion. It now stumbles left and right, so that one might believed it drunk with alcohol. During the fit it scarcely lets itself be approached by its master, whom it regards with a threatening air. Other attacks then occur, during which it involuntarily expels solid and liquid excrementitious matters, whilst it indulges in a furious and noisy run. Suddenly it stops, seized with a slight nervous trembling, and as it shivers one would say it had cold. The strange way in which it then begins to sniff the air causes the belief that there is also a disordered sense of smell. Now, abruptly springing up, seized with a great terror, and with its tail between its legs, it runs away crying, and hastens to take refuge in dark corners or under the furniture, or it seems to defend itself by barking at an imaginary phantom. It is these dreadful visions which above all predominate, but they soon give way to attacks of rage, or to a stupid desire to make a noise. The fear is very great and the sensibility overexcited, and any object, however slight, such as a small piece of wood, thrown to the dog during the fit causes it to utter loud cries. When it begins to drink the reflections from the water as it is agitated appear to make the animal afraid and it shrinks away. Later it is seized with an attack of mastication, and flakes of white foam issue from its mouth. The salivary secretion continues very excessive, though intermittently, during three days, in the course of which the dog is observed to slumber momentarily, with open eyes; then abruptly, at the end of some seconds, it moves as though awaking; in brief, *it has lapses of consciousness*. This is very characteristic. All these symptoms are repeated during six to eight days, after which the dog is restored to health. Subsequently it remains for some time subject to epileptic-like fits, but the animal, which had become of a gloomy and sad disposition, recovers little by little its normal state.

The condition produced in the dog by the 8 milligrams of substance lasted a period of six days. On the seventh day food was taken and the animal had fair control of his muscles. On the tenth day he seemed to have fully recovered his previous condition, except for weight.

Kobert [37] also speaks of the remarkable effect of the crude drug on dogs and states that it might contain a compound of therapeutic value. With the beginning of the next fruiting season, when larger quantities will be available, the investigation of this plant will be continued.

Without doubt *Rourea erecta* is poisonous in small doses to carnivorous animals. *Rourea volubilis* may not be poisonous, or the active substance may not be present in so large quantities. An attempt will be made to obtain specimens of the latter for examination in order that its properties may be compared with those of *R. erecta.*

[37] Kobert, R., *Centralbl. f. klin. Med.* (1893), 14, 927.

### HYMENODICTYON EXCELSUM WALL (?)[38] (RUBIACEÆ)

*Tubo-bató* (Tagbanua in Palawan), *abar* (Il. in Abra and Ilocos Sur), *alegango* (T. in Bulacan), *mag-talisay* (V. in Guimaras Island), *balangcari* (T. in Nueva Ecija), *malatabaco hibao* (T. in Rizal), and *huliganga* (T. in Batangas).

This rubiaceous plant, which once acquired some renown in India, Blanco erroneously classified as *Exostemma philippicum.*

In view of the opinion of some writers who claim the possibility of using its bark as a substitute for quinine as a febrifuge, a chemical trial was made to obtain the hymenodictyonine, the alkaloid obtained by Naylor[39] from the Indian *Hymenodictyon excelsum.* We were unable to isolate the alkaloid described by Naylor.

The fact that the alkaloid that apparently characterizes the Indian *Hymenodictyon excelsum* Wall. was not found in the bark of Philippine *Hymenodictyon* raises some doubt as to whether or not the plant found in the Philippines belongs to that species. Our identification of the Philippine material as *H. excelsum* follows the determination of Philippine material made at Kew, England.

Following we quote what Dymock writes in his vegetable materia medica of Western India:[40]

> In 1870, Broughton examined the fresh bark of one of the Hymenodictyons, and found that the bitter taste was due to the existence of aesculin, and that the bark when dry was almost tasteless owing to the transformation of that substance into *aesculetin* the decomposition having been induced by contact with decaying organic matter.

The fact here mentioned that the bark when dry lost its bitterness leads us to suppose that it was not that of *H. excelsum* but of *H. obovatum,* the dry bark of the former tree being extremely bitter.

#### CHEMICAL EXAMINATION OF HYMENODICTYON EXCELSUM

Both the fresh and dried bark were used in these analyses. The fresh bark treated with water and heated to 90° C. gives a highly satisfactory extraction of the active principle. The fluorescent filtrate was clarified with neutral lead acetate

[38] The Philippine plant is a *Hymenodictyon* very closely allied to, if not identical with, *H. excelsum* Wall. A critical comparison with type material will be necessary definitely to determine whether one or two species are involved.

[39] Naylor, W. A. H., *Pharm. Journ.* (1883–4), 14, 311.

[40] Dymock, W., The Vegetable Materia Medica of Western India. 2d. ed. (1885), 404.

according to the method of van Rijn [41] and was evaporated. A crystalline substance was obtained. This compound reduced Fehling solution on prolonged boiling. Tests for alkaloids by the usual methods showed no such compounds present.

Four hundred grams of fresh bark were macerated with hot water, the extract was filtered, and the filtrate was evaporated to a thick syrup under vacuum and then repeatedly extracted with 80 per cent ethyl alcohol. A yield of 11.091 grams of pale yellow crystals was obtained. When purified by recrystallization from hot dilute alcohol, this compound forms a mass of colorless crystals by quick crystallization and groups of plates or flat prisms by slow crystallization.

Four hundred grams of quickly dried bark were first extracted by petroleum ether and then by ether. Neither of these solutions contains alkaloids and but slight traces of the above-mentioned compound. The residual plant material was treated with a mixture of 90 per cent alcohol and chloroform and filtered hot. This solution treated with water liberates a considerable amount of crystallizable compound of the same nature as that obtained by the method of van Rijn. It is purified by repeated crystallization from dilute alcohol.

The nature of the active principle of *Hymenodictyon excelsum* seems to be accepted by some as æsculin and by others as an alkaloid. Broughton [42] found æsculin in *Hymenodictyon excelsum* by extracting the bast material with hot water, evaporating the filtered solution, mixing it with magnesia, and evaporating and extracting the residual mass with strong alcohol. By concentrating this filtrate and letting it stand twelve hours, he obtained prismatic crystals which on acid hydrolysis gave æsculetin and a sugar. Broughton also found that the bitter taste is not obtained from the dry bark, and he concludes that in drying the æsculin is converted to æsculetin.

Naylor [43] denies Broughton's conclusion of the compound being æsculin and alleges that *Hymenodictyon excelsum* contains an alkaloid which he terms "hymenodictyonine." Naylor's second method of extraction and the one he recommends is as follows:

Mix the ground bark with ¼ weight of lime and convert into a thick paste with $H_2O$, dry and exhaust the mixture with chloroform. Extract the chloroform mixture with dilute sulphuric acid solution, precipitate the alkaloid with sodium hydroxide solution, and extract with ether. Repeat to purify.

[41] Op. cit., 288.

[42] Broughton, *Jahresber. d. Pharmacog., Pharm., u. Toxic.* (1868), **3**, 81.

[43] Naylor, W. A. H., *Pharm. Journ. & Trans.* (1883–4), **14**, 311.

He prepared a crystalline hymenodictyonine by extremely slow evaporation of an ethereal solution. Analysis of the compound showed it to be dibasic, probably a tertiary diamine, with the formula $C_{32}H_{40}N_3$ and bearing relationship to either berberine or cinchona (paricine). Some further properties which he attributes to the hymenodictyonine are these:

*Description of the Alkaloid.*—In the moist condition, as obtained by precipitation with caustic alkali, it is a gelatinous mass of a cream colour and greedy of water, which it retains with extreme tenacity. By exposure it shortly acquires a decided yellow colour, which deepens with increase of temperature and passes into a light brown at 100°C. It has a persistently bitter taste, which is more quickly perceived when in solution than when in the solid state. It is readily soluble in alcohol, ether, chloroform, benzol, and light petroleum spirit. On evaporation of its ethereal solution at a slightly elevated temperature it separates out in the form of oily drops. If the heat be continued beyond that required for the complete evaporation of the ether, the oily drops coalesce and the whole assumes the character of a soft sticky resin. It commences to fuse at 66°C., and at 70°C. it will flow with ease sufficient to admit of its transference to another vessel. It neutralizes acids completely and the solutions are not fluorescent. It refuses to yield crystallizable salts with nitric, hydrochloric, acetic, sulphuric, phosphoric and hydrobromic acids. Its solution in hydrochloric acid is precipitated by nitric acid, sodium nitrate and phosphate, potassium iodide, ferro and ferricyanide and bichromate, and mercuric chloride, in addition to the usual alkaloidal reagents. Potassium sulphocyanide added in excess to a neutral solution of the base in acetic acid gives reddish-yellow oily drops. A feebly acid solution gives with bromine a bright yellow precipitate and with solution of chlorinated lime a white precipitate unaffected by ammonia. A two per cent solution in 90 per cent alcohol is optically inactive.

Naylor [44] did some work on *Hymenodictyon excelsum* prior to that already quoted. The difficulties encountered here were cleared up in the later work, in which radical changes were made in his methods of analysis and certain mistakes corrected.

It is of interest to note that Naylor makes no mention of any fluorescence existing in any of his original solutions. In all the solutions from the material furnished in this investigation such a phenomenon was a marked factor in determining the relative extractive power of the solvent.

Comparative tests on the products isolated from Philippine *Hymenodictyon excelsum* and on specimens of pure æsculin show them to be very similar in many of their reactions, and confusion as to the identity of the compound could easily arise.

Some differences exist in the literature regarding the melting point of æsculin.

[44] Naylor, W. A. W., ibid. (1883), 13, 817; (1884), 15, 195.

Zwenger [45] claims that it melts at 160° C. with loss of water, and if heated over the melting point and then cooled, it crystallizes again free from its water of crystallization.

Schiff [46] reports having had æsculin with 1.5 and with 2 molecules of water of crystallization and that heating it above 160° C. gives a compound which melts at 204° to 205° C. Heated to 230° C., the compound breaks down into æsculetin. According to Schiff [47] æsculin loses part of its water of crystallization at 130° C. and the remaining 1.5 molecules at 160° to 165° C.

The melting point is listed in Beilstein as 165° C. Melting points made by us on Kahlbaum's æsculin show æsculin to melt at 165° C., but immediately to solidify and then to melt at 200° to 205° C. with decomposition. In some cases where the heating was rapid no melting resulted at 165° C., only a slight softening was noticeable, and the only melting point observed in such cases was the higher one.

The compound obtained from the Philippine *Hymenodictyon excelsum* by the various methods gives melting points varying from 195° to 205° C. No melting point or softening was observed at 165° C. A mixture of this compound with æsculin (Kahlbaum) melted at 169° C. and when heated to a higher temperature did not again solidify and then melt in the vicinity of 200° C., as does pure æsculin. It is much less soluble in water than is æsculin. It is not hydrolyzed to æsculetin by dilute hydrochloric or sulphuric acid as is æsculin. It is precipitated by neutral lead acetate, [48] while æsculin is not.

The compound was recovered from the lead precipitate by treatment with hydrogen sulphide. The melting point was sharp at 203° C. This is the original compound. No separation had taken place as we thought might be accomplished were the substance a mixture of æsculin and æsculetin, which seemed possible from the reported work of Broughton [49] on the hymenodictyons. The compound is apparently a definite compound and not a mixture. It has properties which distinguish it from æsculin and from æsculetin, which is formed from æsculin by hydrolysis with dilute acids or emulsin.

[45] Zwenger, C., *Ann. d. Chem.* (Liebig) (1854), 90, 65.

[46] Schiff, H., *Ber. d. deutsch. chem. Gesell.* (1881), 14, 303.

[47] Schiff, H., ibid. (180), 13, 1952.

[48] Our clarification of the extract from the plant by means of neutral lead acetate did not precipitate the compound, as only enough acetate was added to clarify the solution.

[49] Dymock, W., The Vegetable Materia Medica of Western India. 2d ed. (1885), 404.

The compound resembles æsculin by the fluorescence in solution of carnelian yellow by transmitted light and of opalescent blue by reflected light. The intensity of the fluorescence is increased by the addition of ammonium hydroxide or other bases and is changed by the addition of acids to a purplish fluorescence of less intensity. Tests for nitrogen were negative.

The compound is acid in solution and gives the blood red color produced by æsculin [50] when treated with nitric acid and ammonium hydroxide. A bromine product is formed when the compound is treated with bromine solution at room temperature. Crystallization was effected in acetic acid by warming on the steam bath. The product was readily soluble in acetic acid and difficultly soluble in alcohol. The dry substance reacts positively for bromine and negatively for nitrogen. The melting point is 235° C. with decomposition. The melting point of tribromæsculetin is 240° C. (not sharp, Beilstein), while monobromæsculin melts at 193° to 195° C. The compound may have been hydrolyzed to æsculetin by the above treatment and tribromæsculetin formed, or it may be the brom derivative of a different compound. A brom compound prepared by treatment of an acetic acid solution with bromine kept at the temperature of melting ice gave a compound with a melting point of 238° C.

An acetyl derivative formed by treatment of the compound with acetic anhydride with gentle heating over a small flame had a melting point of 177° C. It is readily soluble in acetic acid and is thrown out by addition of water. When carefully crystallized, it is obtained in the shape of rhombic prisms and plates. The diacetyl derivative of æsculin melts at 130° C., and diacetyl æsculetin melts at 133° to 134° C.

The compound isolated from the Philippine *Hymenodictyon* is neither æsculin nor æsculetin. We believe it to be identical with β-methyl-æsculetin found by Schmidt [51] in the roots of *Gelsemium sempervirens.* He describes β-methyl-æsculetin as crystallizing in colorless, odorless, tasteless needles, which are soluble in ether, chloroform, and hot water. It gives a deep fluorescent solution with alkalies; a yellowish red solution with nitric acid, which changes to blood red on the addition of ammonium hydroxide and possesses a melting point of 202° to 203° C.; and a green color with ferric chloride. It reduces Fehling solution when warmed. With a solution of gold chloride it gives a red, and with potassium permanganate a green, color.

[50] van Rijn, op. cit., 288.

[51] Schmidt Ernst, *Arch. d. Pharm.* (1898), **236**, 324.

By treatment with hydriodic acid according to the method of Zeisel, β-methyl-æsculetin splits into methyl iodide and æsculetin.

The compound isolated from *Hymenodictyon* gives the above reactions, and we, therefore, announce the presence of β-methyl-æsculetin in the Philippine *Hymenodictyon excelsum.*

SUMMARY

The following-named plants were examined for physiologically active constituents with the results noted: *Lophopetalum toxicum* Loher contains a saponin which is poisonous in small quantities. *Erythrophloeum densiflorum* (Elm.) Merrill contains tannins, but no substances with any marked physiological properties. *Quisqualis indica* L. contains an oil in the seeds which has purgative properties; a gum in the stems which is inactive physiologically, but gives some of the chemical tests of the alkaloids; and a considerable amount of potassium sulphate. *Tylophora brevipes* (Turcz.) F.-Vill. contains an alkaloid identical in properties with tylophorine found by Hooper in *Tylophora asthmatica* growing in India. *Toddalia asiatica* (L.) Kurz contains the alkaloid berberine. *Lunasia amara* Blanco contains an alkaloid identical in properties with lunasine found by Boorsma in *Lunasia costulata* Miq. in Java. *Rourea erecta* (Blanco) Merrill is physiologically active toward the Carnivora, but inactive toward the Herbivora; the active principle could not be isolated, but further attempts will be made to isolate this when larger quantities of material are available. *Hymenodictyon excelsum* Wall. (?) contains β-methyl-æsculetin. It differs from *H. excelsum* of India, since the latter contains æsculin, according to Broughton, while Naylor claims to have found an alkaloid, which has been named hymenodictyonine by him.

## ILLUSTRATIONS

### PLATE I

FIG. 1. Crystals of the hydrochloride of the alkaloid from *Tylophora brevipes.*

2. Crystals of the free alkaloid from *Toddalia asiatica.*

### PLATE II

FIG. 1. Crystals of the nitrate of the alkaloid of *Toddalia asiatica* from absolute alcohol.

2. Same, crystallized from water.

### PLATE III

FIG. 1. Crystals of the free alkaloid from *Lunasia amara* by quick crystallization from alcohol.

2. Same, crystallized from amorphous substance on long standing in vacuo.

### PLATE IV

FIG. 1. Crystals of the hydrochloride of the alkaloids from *Lunasia amara.*

2. Crystals of the nitrate of the alkaloid from *Lunasia amara.*

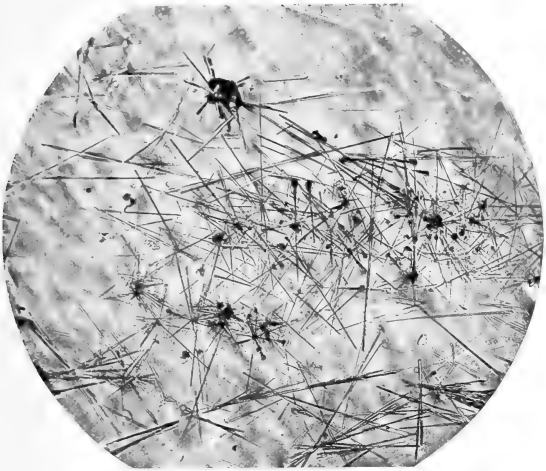

Fig. 1. Crystals of the hydrochloride of the alkaloid from Tylophora brevipes.

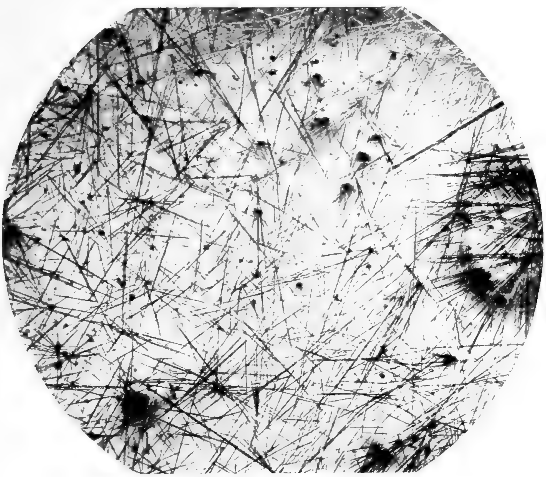

Fig. 2. Crystals of the free alkaloid from Toddalia asiatica.

PLATE I.

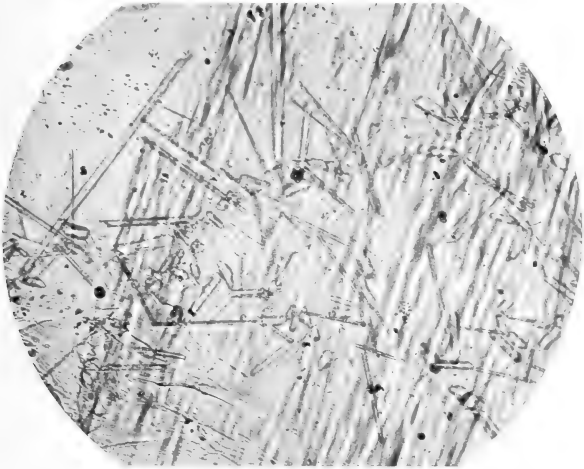

Fig. 1. Crystals of the nitrate of the alkaloid of Toddalia asiatica from absolute alcohol.

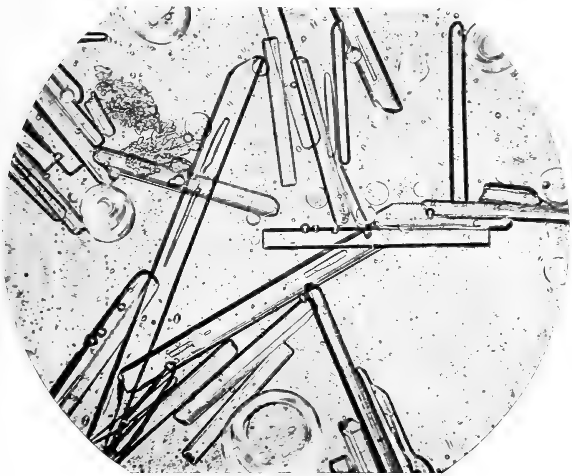

Fig. 2. Same, crystallized from water.

PLATE II.

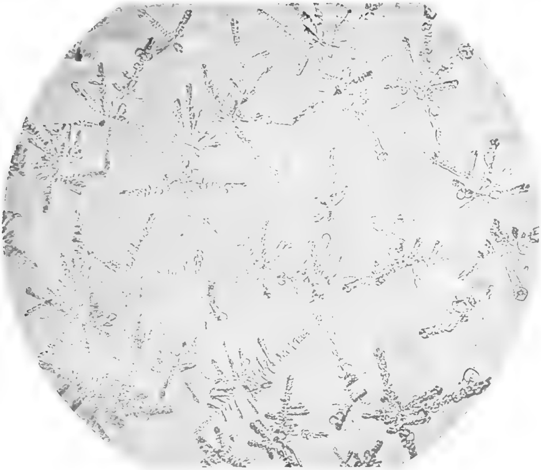

Fig. 1. Crystals of the free alkaloid from Lunasia amara by quick crystallization from alcohol.

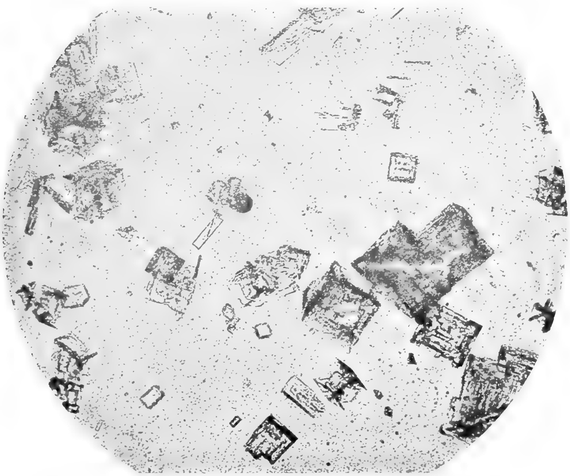

Fig. 2. Same, crystallized from amorphous substance on long standing in vacuo.

PLATE III.

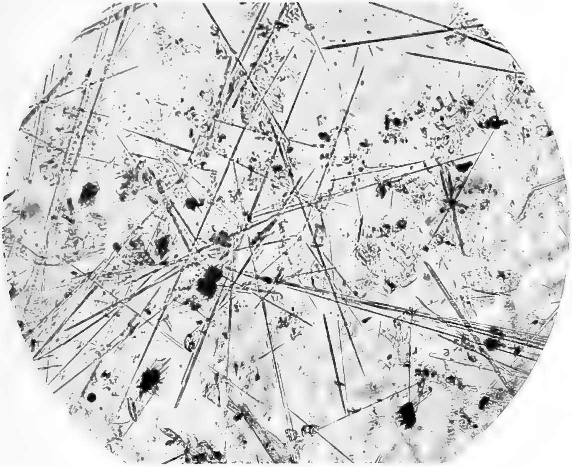

Fig. 1. Crystals of the hydrochloride of the alkaloids from Lunasia amara.

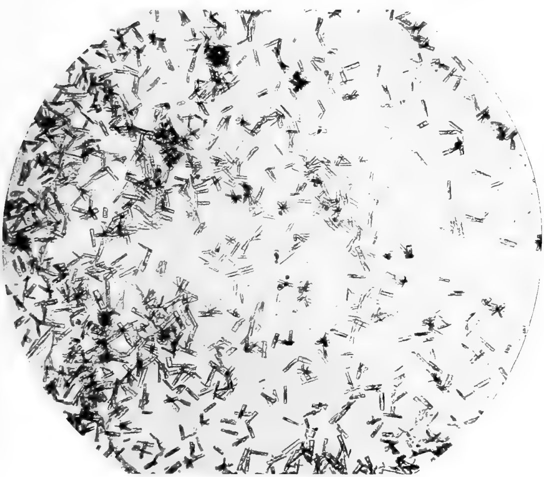

Fig. 2. Crystals of the nitrate of the alkaloid from Lunasia amara.

PLATE IV.

# THE ANTINEURITIC PROPERTIES OF THE INFUSORIAL EARTH EXTRACT OF THE HYDROLYZED EXTRACT OF RICE POLISHINGS [1]

By Harvey C. Brill

*(From the Laboratory of Organic Chemistry, Bureau of Science, Manila)*

The Bureau of Science prepares approximately forty liters of extract of rice polishing for monthly distribution by the Liga Nacional para la Proteccion de la Primera Infancia for use in the treatment of infantile beriberi.

In the past considerable difficulty has been experienced in preventing the fermentation of this solution after bottling. The practice of fractional sterilization at 70° C. prevents this fermentation, and the bottled extract remains sweet and unfermented indefinitely. But when the 50 cubic centimeter bottles of extract are distributed for use, fermentation often occurs due to the withdrawal of a portion of the contents, contamination with yeast cells, and the incubation at room temperature.[2] In an endeavor to prevent such fermentation, any one of several means might be employed: (1) A preservative might be added. Most, if not all, preservatives have a physiological action and the administration of them to people who are already in an unhealthy physical condition is to be avoided, if possible. (2) Smaller bottles of the extract might be distributed. There are several objections to this procedure. The cost of containers and the cost of handling would be greater; a smaller bottle would hold an amount insufficient to effect a cure or even improvement in some cases. The patient or the family of the patient would either need to make several trips to the dispensary or take more than one bottle of the extract. Either practice is to be avoided, if possible, on account of the difficulty of following the history of the case and the waste of extract that would result. (3) The extract might be issued in some form that would avoid the risk of fermentation.

Infusorial earth has the power of extracting the salts of al-

[1] Received for publication April, 1917.

[2] The class afflicted with beriberi usually has no facilities for keeping its food and medicine cool.

kaloids from acid solutions.[3] This property of infusorial earth caused Seidell [4] to attempt the extraction of vitamine from brewer's yeast.[5] The above-named investigator obtained yeast from the breweries and subjected it to pressure to free it from the beer retained in it. The yeast was then autolyzed at a temperature of 37.5° C. and filtered. The brown filtrate was active, protecting a pigeon from the onset of polyneuritis for several months when administered in doses of 1 cubic centimeter on alternate days. This active liquid was treated with a prepared hydrous aluminium silicate (Lloyd's reagent) in the proportions and with the results given in Table I.

TABLE I.—*Extraction of yeast liquid with Lloyd's reagent.*

| Quantity of yeast liquid. | Quantity of Lloyd's reagent. | Activity of filtrate. | Activity of extract. |
|---|---|---|---|
| *cc.* | *g.* | | |
| 1,000 | 200 | Inactive | Active. |
| 1,000 | 20 | Fairly active | Do. |
| 1,000 | 40 | Slightly active | Do. |
| 1,000 | 50 | Practically inactive | Do. |

Twenty grams of Lloyd's reagent were insufficient to extract all the vitamine from a liter of yeast liquid; 40 grams left a small proportion remaining in the filtrate. After extraction with 50 grams of Lloyd's reagent, the filtrate possessed only slightly protective powers from polyneuritis when administered to pigeons.

## EXPERIMENTAL PART

Because of the difficulty experienced in keeping the extract of rice polishings sterile, it was decided to investigate the possibility of extracting the hydrolyzed extract of rice polishings with infusorial earth. This infusorial earth was obtained from Japan. Its absorptive powers are less than those of Lloyd's reagent. Under the conditions described by Lloyd for testing the efficiency of his reagent, Japanese infusorial earth reacted as follows:

[3] Lloyd, John U., *Journ. Am. Pharm. Assoc.* (1916), 5, 381.

[4] Seidell, Atherton, *U. S. Pub. Health Rep.* (1916), 31, 364.

[5] Brewer's yeast contains the highest percentage of any of the known sources of vitamine. As it is a waste product in the breweries, it is also a cheap source of vitamine.

TABLE II.—*Absorptive power of Japanese infusorial earth for morphine bisulphate.*[a]

| Quantity of infusorial earth used. | Result with Mayer's reagent on the filtrate. |
|---|---|
| *g.* | |
| 0.50 | Not opalescent. |
| 0.40 | Slightly opalescent. |
| 0.35 | Do. |
| 0.30 | Do. |
| 0.25 | Strongly opalescent. |

[a] Five cubic centimeters of a 1 per cent solution of morphine sulphate diluted to 80 cubic centimeters. Lloyd reports his reagent to have an absorptive power of 8 grams of earth to 1 gram of morphine bisulphate. This is nearly the same proportion given by the Japanese earth. The latter has an absorptive power of 10 grams of earth to 1 gram of morphine bisulphate.

The alcoholic extract[6] of rice polishings was hydrolyzed by heating with sulphuric acid in the manner described by Williams and Saleeby.[7] One 500 cubic centimeter portion of this hydrolyzed extract was treated with 50 grams of the Japanese infusorial earth with shaking at intervals for a period of one hour. The mixture was allowed to subside, and the supernatant liquid was siphoned off. The infusorial earth was then placed on a suction funnel and washed with a 5 per cent sulphuric acid solution and finally dried. A second 500 cubic centimeters portion was treated with 25 grams of infusorial earth in a similar manner. The extracts, when dry, were placed in capsules for administration. The 50-gram sample, hereafter referred to as *D*, weighed 95 grams and filled 174 capsules, or each capsule represented the extract from 2.9 cubic centimeters of solution. The 25-gram sample, hereafter referred to as *E*, weighed 49 grams and was placed in 135 capsules, or each capsule represented the extract from 3.7 cubic centimeters of solution. The filtrate from *D* was bottled, subjected to fractional sterilization, and marked *B;* the filtrate from *E* was bottled, subjected to fractional sterilization, and marked *C*. The original hydrolyzed

[6] This extract is made by treating 25 kilograms of rice polishings with 5 demijohns of 25 per cent alcohol and later pressing this. The extract is evaporated at a low temperature, the fat is separated, and alcohol is added to precipitate the albuminous and other matter, and again the extract is evaporated. The solution is concentrated, so that 1 cubic centimeter of extract is equivalent to 15 grams of rice polishings.

[7] Williams, R. R., and Saleeby, N. M., *This Journal, Sec. B* (1915), **10**, 106.

extract of rice polishings is designated as *A* throughout this article.

Two methods are applicable for the determination of activity in these extracts, namely, their protective property from the onset of polyneuritis in chickens fed on polished rice and their curative property when administered to chickens suffering from polyneuritis. Both methods were used for testing these extracts. Twelve chickens were placed on an exclusive diet of white rice and treated in the manner hereafter described. Two chickens had no treatment, but served as controls on the rice used. When polyneuritis became evident, they were treated with some one of the extracts, *A*, *B*, *C*, *D*, or *E*. Two chickens were given 3 cubic centimeters of *A* three times a week; two received 3 cubic centimeters of *B* three times a week; two received 3 cubic centimeters of *C* three times a week; two received one capsule of *D* three times a week; while two received one capsule of *E* three times a week. The experiments extended over a total period of one hundred eighty-six days. Table III gives the history of the chickens fed on polished rice. These chickens had no treatment until polyneuritis had set in. They were then treated as described in the table until their condition improved, when the treatment was discontinued.

TABLE III.—*History of control chickens.*

| No. of chicken. | Days before onset of polyneuritis. | Total number of days on polished rice. | Treatment. | Number of treatments. | Total loss in weight. | Results and remarks. |
|---|---|---|---|---|---|---|
| | | | | | *P. ct.* | |
| 1 | 23 | 28 | None | none | 27 | Died at end of twenty-eight days. |
| 2 | 40 | | 3 cc. of *A* on alternate days. | 3 | | Improved; treatment discontinued. |
| 2 | 69 | 186 | do | 2 | 36 | Improved; treatment discontinued. Living at end of experiment. |
| 3 | 35 | | 1 capsule of *D* on alternate days. | 2 | | Improved; gained weight after treatment. Treatment discontinued. |
| 3 | 18 | 130 | do | 3 | 28 | Improved; living at end of experiment. |

The weight of the chickens recorded in Table III decreased when polyneuritis set in. When treated, their weight increased at once. This increase amounted to as much as 20 per cent in some cases.

In order that a check might be kept on the activity of the original extract of rice polishings, two chickens were treated with 3 cubic centimeters of *A* on alternate days.

TABLE IV.—*History of chickens treated with 3 cubic centimeters of A on alternate days (three times weekly).*

| No. of chicken. | Days before onset of polyneuritis. | Total number of days on polished rice. | Treatment. | Number of treatments. | Total loss in weight. | Results and remarks. |
|---|---|---|---|---|---|---|
| | | | | | P. ct. | |
| 1 | 87 | 92 | No extra treatment | regular. | 50 | Died after refusing to eat for several days. |
| 2 | ------- | 73 | do | regular. | 20 | Died without any symptoms of polyneuritis. |
| 3 | ------- | 70 | do | regular. | 13 | Living at end of experiment in good health. |
| 4 | 15 | ------- | 2 cc. of *A* daily | 2 | ------- | Improved. |
| 4 | 12 | ------- | do | 3 | ------- | Do. |
| 4 | 5 | ------- | do | 7 | ------- | Do. |
| 4 | 7 | 70 | do | 10 | 45 | Living at end of experiment, but in enfeebled condition. |

Three cubic centimeters of extract of rice polishings on alternate days were insufficient to prevent the onset of polyneuritis in chickens 1 and 4, but the extract prolonged the period of good health. Two cubic centimeters of *A* given daily for several days improved the condition of the chickens to such as extent that they could be again placed on the original treatment.

To determine if 50 grams of infusorial earth would extract all the active substance from 500 cubic centimeters of hydrolyzed extract of rice polishings, the experiments recorded in Tables V and VII were planned.

TABLE V.—*History of chickens treated with 3 cubic centimeters of B on alternate days (three times weekly).*

| No. of chicken. | Days before onset of polyneuritis. | Total number of days on polished rice. | Treatment. | Number of treatments. | Total loss in weight. | Results and remarks. |
|---|---|---|---|---|---|---|
| | | | | | P. ct. | |
| 1 | 101 | 104 | 1 capsule of *D* on alternate days. | 2 | 46 | Was in serious condition before it was reported. Died at end of one hundred four days. |
| 2 | 25 | 56 | do | 5 | 34 | Improved; living at end of experiment. |
| 3 | ------- | 186 | None | none | 34 | Living at end of experiment. |

Of the three chickens treated one showed signs of polyneuritis at the end of one hundred one days, the second at the end of twenty-five days, while the third was still healthy at the end of one hundred eighty-six days. The vitamine has not been entirely extracted, as *B* still has protective properties.

In the comparison made on morphine bisulphate, the Japanese infusorial earth compared favorably in absorptive powers with Lloyd's reagent, but Seidell found that 50 grams of Lloyd's reagent extracted all the vitamine from 1 liter of autolyzed yeast liquid, while in the above experiment 50 grams of infusorial earth have not extracted all the vitamine from 500 cubic centimeters of extract. The difference in the absorption must be due to the difference in the character of the two solutions. Hydrolyzed extract of rice polishings is a thick, syruplike liquid, which undoubtedly collects on the infusorial earth and renders it incapable of completely extracting the vitamine from the extract, while the yeast extract is no more viscous than water.

When 500 cubic centimeters of extract of rice polishings are treated with 25 grams of Japanese infusorial earth, the filtrate, *C*, still has protective properties similar to those possessed by *B*.

TABLE VI.—*History of chickens treated with 3 cubic centimeters of C on alternate days (three times weekly).*

| No. of chicken. | Days before onset of polyneuritis. | Total number of days on polished rice. | Treatment. | Number of treatments. | Total loss in weight. | Results and remarks. |
|---|---|---|---|---|---|---|
| | | | | | *P. ct.* | |
| 1 | 63 | 186 | 1 capsule of *E* on alternate days. | 3 | 13 | Alive at end of experiment. |
| 2 | 63 | 68 | do | 1 | 41 | Improved, but died four days later. |
| 3 | | 116 | None | none | 16 | In healthy condition at end of experiment. |

The infusorial earth extracts *D* and *E* possess antineuritic properties. The chickens, No. 1, of Table V, and Nos. 1 and 2, of Table VII, were benefited by the administration of *D* when they had contracted polyneuritis. Chickens 1 and 2, of Table VI, and 1, of Table VIII, were benefited by treatment with *E*.

To test the activity of the infusorial earth extracts, the experiments described in Tables VII and VIII were performed.

TABLE VII.—*History of chickens treated with one capsule of D on alternate days (three times weekly).*

| No. of chicken. | Days before onset of polyneuritis. | Total number of days on polished rice. | Treatment. | Number of treatments. | Total loss in weight. | Results and remarks. |
|---|---|---|---|---|---|---|
| | | | | | *P. ct.* | |
| 1 | 155 | 186 | 1 capsule of *D* daily | 20 | 31 | Living at end of experiments. |
| 2 | 70 | 88 | do | 2 | 19 | Improved, but died fifteen days later. |
| 3 | | 90 | None | none | 6 | In healthy condition at end of experiments. |

TABLE VIII.—*History of chickens treated with one capsule of E on alternate days (three times weekly).*

| No. of chicken. | Days before onset of polyneuritis. | Total number of days on polished rice. | Treatment. | Number of treatments. | Total loss in weight. | Results and remarks. |
|---|---|---|---|---|---|---|
| | | | | | *P. ct.* | |
| 1 | 105 | 122 | 1 capsule of *E* daily | 3 | 23 | Improved, but died ten days later. |
| 2 | | 83 | None | none | 26 | Alive at end of experiments. |
| 3 | 81 | 81 | do | none | 46 | Died without any extra treatment. |
| 4 | | 100 | do | none | 23 | Alive at end of experiments. |

## DISCUSSION

The results obtained show that the curative principle is extracted from the hydrolyzed extract of rice polishings by means of infusorial earth, although not by as small a proportion of the earth as was found by Seidell when he used Lloyd's reagent with autolyzed yeast liquor. This partial extraction is undoubtedly due to the character of the extract.

Extract *A*, given on alternate days in doses of 3 cubic centimeters, did not protect the chickens from polyneuritis for the entire period of one hundred eighty-six days. Chicken 1 contracted polyneuritis on the eighty-seventh day, chicken 2 died on the seventy-third, while 4 became sick on the fifteenth day of its confinement or the one hundred thirty-first day of the experiment. An administration of 3 cubic centimeters of *A* on alternate days should be sufficient to protect these chickens. It is

possible that this extract no longer possesses its full curative properties when it ages. Treatment of chicken 4 was begun on the one hundred sixteenth day of the experiment; consequently the extract used had been made for some time. Williams [8] has recently shown that hydroxy pyridines have antineuritic properties, but these curative effects are lost after a solution stands for some time or more quickly when warmed. Evidence that the antineuritic compounds in autolyzed yeast undergo a change probably due to dynamic isomerism has been presented by Williams and Seidell.[9] A preparation from cardiac muscle loses its ameliorative power in a few days.[10] A similar change may be the cause of the apparent lessened activity with age of the hydrolyzed extract used in these experiments.

The method of extraction with infusorial earth appears inapplicable, due to the inability of small quantities of infusorial earth to absorb the total vitamine content of the hydrolyzed extract of rice polishings.

SUMMARY

A study of the antineuritic properties of infusorial earth extracts of the hydrolyzed extract of rice polishings is reported.

Only a part of the vitamine content of the extract was extracted by the proportions of infusorial earth used.

There appears to be a loss of antineuritic power in the extract as it ages.

[8] Williams, R. R., *Journ. Biol. Chem.* (1916), 25, 437.

[9] Williams, R. R., and Seidell, Atherton, ibid. (1916), 26, 431.

[10] Cooper, Evelyn A., *Biochem. Journ.* (1914), 8, 347.

# THE USE OF CHAULMOOGRA OIL AS A SPECIFIC FOR LEPROSY [1]

By HARVEY C. BRILL and ROBERT R. WILLIAMS

*(From the Laboratory of Organic Chemistry, Bureau of Science, Manila)*

Regarding the cure of leprosy by means of chaulmoogra oil, considerable differences of opinion exist. Thompson,[2] of New South Wales, was unable to effect any cures by its use. The Philippine Health Service released twenty-three cases from Culion leper colony about a year ago that had been treated with chaulmoogra oil. No positive claims that it brought about these cures are made by the more judicial members of the Health Service staff, nor can these patients be considered permanently cured until they have been under observation for a longer period of time. However, chaulmoogra oil appears to be the most promising remedy for the treatment of leprosy at present known.

The administration of chaulmoogra oil is accompanied by considerable difficulties. When administered by mouth, nausea and digestive disturbances follow. Given subcutaneously, it is absorbed slowly, since it is a heavy oil; consequently its administration in this manner is painful, due to the pressure on the nerves and the sores that result from the slow absorption. Then not all cases react to the treatment. The nonuniformity of the results that follow its administration may be due to a difference in the quality of the oil or to a variation in the disease itself in different localities.

Crude chaulmoogra oil is usually recommended for use.[3]

The recommendations of those engaged in its administration are strongly in favor of the crude oil, but these opinions may partly be a matter of prejudice. These practicioners undoubtedly have been previously disposed in its favor by their reading, and as observations of leprosy treatment are not very general nor very decisive, and as recovery in any case is slow, decisions as to its efficiency are difficult to form. We must conclude that cases of positive cures by means of chaulmoogra oil are not definitely proved.

[1] Received for publication January 29, 1917.

[2] Report of the Board of Health on Leprosy in New South Wales (1908).

[3] United States Dispensatory. 18th ed. (1899), 1678.

EFFECTIVENESS OF CHAULMOOGRA OIL

Again, standards for determining whether an oil is crude or refined are rather arbitrary, and when applied to an oil such as chaulmoogra, where the previous history of the oil is not known, the difficulty of deciding is still more difficult. An expressed oil would carry with it other substances. For example, when the oil from bitter almonds is expressed, a small amount of the amygdalin of the nuts is carried with the oil. Power and Lees[4] have shown that the chaulmoogra seeds and the hydnocarpus seeds all contain small quantities of a cyanogenetic glucoside that they found to be identical with gynocardin, the glucoside present in *Gynocardia odorata.*

When the oil of these nuts is expressed, minute amounts of the glucoside doubtless accompany the oil; therefore the effectiveness of the crude oil may possibly be due to the presence of the cyanogenetic glucoside. The small amount of the glucoside present would account for the slowness of the action of the oil. The small amount of glucoside that may possibly be present in the oils is shown by the nitrogen content of some chaulmoogra oils in Table I. These data illustrate the maximum possible amount that could be present.

TABLE I.—*Nitrogen content of various chaulmoogra oils.*

| No. of sample.[a] | Nitrogen. | Calculated as gynocardin ($C_{13}H_{19}O_9N + 1.5H_2O$). |
|---|---|---|
| | *Per cent.* | *Per cent.* |
| 1 | 0.01363 | 0.350 |
| 2 | 0.00438 | 0.113 |
| 3 | 0.01380 | 0.355 |
| 4 | 0.01415 | 0.364 |
| 5 | 0.01257 | 0.323 |
| 6 | 0.00670 | 0.172 |
| 7 | 0.01503 | 0.386 |
| 8 | 0.02209 | 0.568 |

[a] For description of samples see Table III.

CONSTITUTION OF THE OIL

The acids of the oils of this family of seeds, *Taratogenos kurzii,*[5] *Hydnocarpus wighttiana, H. anthelmintica,*[6] *H. venenata,*[7]

[4] *Journ. Chem Soc. London* (1905), 87, 349.
[5] Power and Gornall, *Journ. Chem. Soc. London* (1904), 85, 838.
[6] Power and Barrowcliff, ibid. (1905), 87, 884.
[7] Brill, *This Journal, Sec. A,* (1916), 11, 75.

*H. alcalae*, and *Pangium edule*,[8] are peculiar in that they are monobasic unsaturated acids with a ring structure.[9] Chaulmoogric acid is isomeric with linoleic acid ($C_8H_{32}O_2$), but differs from the latter in that it combines with but two bromine or iodine atoms and contains but one ethylenic linking and a closed chain. It is very stable toward alkalies. Heating to 300° C. with alkalies does not decompose it. It is optically active, rotating the plane of polarized light to the right. These properties make it distinct from all other known acids, and one would expect its physiological properties to be different from those of other acids.

Hydnocarpic, the other peculiar acid found in the oil of these seeds, is a lower member of this same series.

Chattopadhyay[10] has taken exception to the conclusions of Power and his coworkers regarding the presence of acids of the nature of chaulmoogric and hydnocarpic in chaulmoogra oil, but his results are not complete enough to substantiate his contention. The results by one of us (Brill) on *H. venenata*[11] are in agreement with those of Power et al., and unless Chattopadhyay can produce results which really contradict those of Power, the results of the latter will continue to be accepted. That the effectiveness of chaulmoogra oil may be due to the presence of free acids has received further confirmation recently by the experiments of Leonard Rogers,[12] who administered the free acids themselves and these in the form of their sodium salts. However, the compound known as antileprol, which is the mixture of the ethyl esters of chaulmoogric and hydnocarpic acids, was without effect when used by the Philippine health authorities. We should expect the ethyl esters to have an effect as powerful as that of the free acids, since they would be readily hydrolyzed in the system. Indeed it is hardly to be expected that the free acids should be so radically different in activity from the glyceryl esters, the neutral oil itself, since the oil when absorbed would be undoubtedly hydrolyzed to some extent in the system. The use of the soluble alkali salts would appear to be more promising on account of their solubility and more ready absorption, and as Rogers obtains promising reactions when a solution of these salts is administered intravenously, they deserve to be tested thoroughly by the various scientists interested in the treatment of leprosy.

The work described in this article was undertaken in the hope

[8] Brill, ibid. (1917), **12**, No. 1.

[9] Barrowcliff and Power, *Journ. Chem. Soc. London* (1907), **91**, 557.

[10] Chattopadhyay, P. C., *Am. Journ. Pharm.* (1915), **87**, 473.

[11] Loc. cit.

[12] *Lancet* (1916), **190**, 288; *Indian Med. Gaz.* (1916), **51**, 195 and 437.

that some light might be thrown on the constituent in chaulmoogra oil that is specific for leprosy; that it might be isolated and that its isolation would simplify the administration of the oil; and that the more concentrated form of the physiologically active substance would bring about speedier improvements in the condition of the patients. While the results have not been entirely successful in this endeavor, yet in the hope that they may give an inspiration to other investigators, and because of the information they give concerning chaulmoogra oil itself, they are presented here.

The administration of the preparations was kindly performed by the Philippine health authorities at the Culion leper colony.

Circumstances were such that in some cases the treatment was not continued over a sufficiently prolonged period, nor were the administrations frequent enough. Denney[13] has described the difficulties of persuading lepers to continue a treatment for any length of time. For this reason some of the fractions hereafter described might show more satisfactory results under more favorable circumstances. The treatment at Culion is entirely voluntary. The leper voluntarily presents himself for treatment, and the treatment is continued only as long as the patient is in the humor for taking it. No coercion can be applied; consequently the health officer is handicapped in his desire for a systematic study of the treatment of leprosy.

TABLE II.—*Constants of various chaulmoogra oils examined by the Bureau of Science.*

| Sample No. | Specific gravity at 30° C. | Specific rotation in chloroform for sodium light. | Acid value cc. 0.1 *N* base. | Saponification value. | Index of refraction. | Iodine value. |
|---|---|---|---|---|---|---|
| 1 | 0.9535 | +52.23 | 5.28 | 196.6 | 1.4755 | 99.3 |
| 2 | 0.9464 | +52.12 | 2.69 | 189.1 | 1.4768 | 101.1 |
| 3 | 0.9492 | +45.69 | 7.19 | 191.6 | 1.4766 | 102.6 |
| 4 | 0.9492 | +57.45 | 9.38 | 196.8 | 1.4730 | 79.6 |
| 5 | 0.9429 | +48.95 | 21.48 | 196.3 | 1.4720 | 100.1 |
| 6 | 0.9487 | +58.20 | 5.63 | 196.2 | 1.4732 | 102.1 |
| 7 | 0.9484 | +48.73 | 1.55 | 210.5 | 1.4755 | 110.4 |
| 8 | 0.9467 | +46.26 | 6.36 | 210.5 | 1.4750 | 104.6 |
| 9 | 0.9470 | +51.60 | 2.80 | 215.0 | 1.4774 | 107.5 |
| 10 | 0.9454 | +47.30 | 5.56 | 203.3 | 1.4762 | 99.5 |
| Maximum | 0.9535 | +58.20 | 21.48 | 210.5 | 1.4774 | 110.4 |
| Minimum | 0.9429 | +45.69 | 1.55 | 189.1 | 1.4720 | 97.6 |
| Average | 0.9471 | +50.81 | 6.79 | 200.4 | 1.4751 | 102.4 |

[13] Denney, Oswald E., *This Journal, Sec. B* (1915), **10**, 357.

For comparative purposes the constants of chaulmoogra oil used in this experimental work and of other samples of chaulmoogra oil that have been examined in the Bureau of Science are inserted.

DESCRIPTION OF SAMPLES OF CHAULMOOGRA OIL

*Sample 1.*—This oil was obtained from the Philippine Health Service from the stock used by them in the treatment of the lepers at Culion. It was a greenish yellow limpid oil (30°C.) with a characteristic odor.

*Sample 2.*—This oil was extracted from seeds by means of petroleum ether. The oil was liquid (30° C.) ; it was somewhat lighter in color than sample 1, but had the same odor. The seeds were obtained from H. G. Carter, economic botanist to the Botanical Survey of India, Calcutta, India, and were labeled "chaulmoogra seed—*Taraktogenos kurzii.*"

*Sample 3.*—This is an oil purchased from the German Dispensary, Manila. The oil was of the same color and odor as sample 1, but differed from the preceding in that it had a small quantity of solid particles deposited, about two parts per hundred.

*Sample 4.*—This is a sample of oil purchased from the Botica de Santa Cruz, Manila, and marked "Aceite de Chaulmugra." The sample was practically identical with sample 1 in appearance and other properties.

*Sample 5.*—This sample was purchased from the Botica de Santa Cruz. It bore the following on its label:

"Chaulmoogra oil." The fixed oil expressed from the seeds of *Gynocardia odorata* R. Brown natural order Bixaceæ. Should the oil become solidified from cold, it may be readily liquified by placing the container in warm water.

Dose 10 to 20 minims (0.6 to 1.3 cc.). Guaranteed under the Food and Drugs Act, June 30, 1906, guaranty No. 6.

This oil was so nearly solidified at the ordinary temperature (30° C.), that it would not readily pour.

*Sample 6.*—This oil was submitted by the Philippine Health Service for test to determine its purity. The sample was liquid and possessed the odor and color of sample 1.

*Sample 7.*—This oil was expressed from seeds purchased through the Department of Agriculture, Assam, Seed Depot Gauhati. They were marked "*gynocardia odorata,*" but were sold to the Bureau of Science in response to a request for chaulmoogra seeds. The oil was a heavy, limpid oil, darker in color than sample 1, but with the same characteristic odor.

*Sample 8.*—This oil was submitted by the Philippine Health

Service for testing as to purity. It was marked: "Finest oil of Chaulmoogra, Stanistreet Brand." It is very similar in properties to sample 7.

*Sample 9.*—This oil is identical in all respects with sample 7, being obtained by expression from seeds from Assam, marked "*Gynocardia odorata.*"

*Sample 10.*—This oil was submitted by the Philippine Bureau of Supply for testing as to purity. It was marked: "Crude Chaulmoogra Oil. A. S. Watson, Hongkong China." The oil was very similar to sample 1.

A survey of the constants of the oils described above shows that they are different from the constants given by Power and Barrowcliff [14] for the oil from *Gynocardia odorata* and that the name *Gynocardia odorata* used for some of the oils examined by us is incorrect, but that they are in substantial agreement with their results for the chaulmoogra and the hydnocarpus oils.

## CHEMICAL EXAMINATION OF CHAULMOOGRA OIL

A more thorough chemical examination of chaulmoogra oil was made for the purpose of substantiating the results of either Power or those who disagree with him. For this examination samples 2 and 5 were chosen. They were saponified with alcoholic potash, and the free acids were obtained by acidification and extraction with ether. Table III gives the properties of the free acids.

TABLE III.—*Properties of the free acids of chaulmoogra oil.*

| | Sample No.— | |
|---|---|---|
| | 2 | 5 |
| Specific rotation in chloroform for sodium light at 30° C | +54.00 | +47.40 |
| Iodine value | 101.3° | 99.7° |
| Acid value cc | [a] 35.31 | [a] 34.95 |
| Melting point °C | 38–39 | 39–40 |

[a] 0.1 *N* base.

These acids were treated in the manner adopted by Power for the separation of chaulmoogric and hydnocarpic acids.

Not much difficulty was experienced in obtaining a body from No. 5 that melted at 67° to 68°C. when recrystallized from alcohol, but considerable difficulty was experienced in purifying the fraction from No. 2 sufficiently to raise its melting point to

[14] *Journ. Chem. Soc. London* (1905), 87, 887.

67° to 68° C. The properties of these acids are tabulated in Table IV. When the residue of acids after the separation by means of crystallization from alcohol was treated with barium acetate, four fractions were obtained. These had the melting points noted in Table IV.

TABLE IV.—*Melting point of acids obtained by treatment with barium acetate.*

| | Sample No.— | |
|---|---|---|
| | 2 | 5 |
| | °C. | °C. |
| Melting point of fraction 1 | 36–37 | 47–48 |
| Melting point of fraction 2 | 40–41 | 38–39 |
| Melting point of fraction 3 | 39–40 | 39–40 |
| Melting point of fraction 4 | 37–38 | 34–35 |

NOTE.—Fractions 2 and 3 were in both cases united, and the combined portions were recrystallized from alcohol, discarding the portion first crystallizing out. They were then again converted into the barium salts, the acids set free, and again crystallized from alcohol. The melting points correspond to the melting point of hydnocarpic acid, 59° to 60° C.

TABLE V.—*Saponification values of acids isolated from chaulmoogra oil.*

| Sample. | Quantity. | 0.1 *N* base required for neutralization. | Saponification value.[a] |
|---|---|---|---|
| | *g.* | *cc.* | |
| 2 for chaulmoogric acid | 1.1454 | 40.92 | 200.5 |
| 5 for chaulmoogric acid | 1.0587 | 38.13 | 202.4 |
| 2 for hydnocarpic acid | 1.9205 | 76.21 | 222.7 |
| 5 for hydnocarpic acid | 2.8560 | 110.82 | 218.2 |

[a] Theoretical saponification value for chaulmoogric acid, $C_{17}H_{31}COOH = 200.5$; for hydnocarpic acid, $C_{15}H_{27}COOH = 222.7$.

TABLE VI.—*Specific rotation in chloroform at 30° C/D of acids isolated from chaulmoogra oil.*

| Sample. | Quantity in 25 cc. chloroform. | Rotation in cm. tube. | Specific rotation.[a] |
|---|---|---|---|
| | *g.* | *Degrees.* | *Degrees.* |
| Chaulmoogric acid: | | | |
| 2 | 1.8120 | +2.14 | +59.05 |
| 5 | 1.4416 | +1.68 | +58.10 |
| Hydnocarpic acid: | | | |
| 2 | 2.6740 | +7.24 | +67.70 |
| 5 | 1.5545 | +4.20 | +67.60 |

[a] Found by Power for chaulmoogric acid, 58.6°; for hydnocarpic acid, 68.1°.

TABLE VII.—*Iodine value of acids isolated from chaulmoogra oil.*

| Sample. | Quantity. | 0.1 *N* iodine solution used. | Iodine value (Hanus).[a] |
|---|---|---|---|
| | *g.* | *cc.* | |
| Chaulmoogric acid: | | | |
| 2 | 0.1806 | 12.73 | 89.5 |
| 5 | 0.1558 | 11.13 | 90.7 |
| Hydnocarpic acid: | | | |
| 2 | 0.2250 | 17.71 | 100.2 |
| 5 | 0.1625 | 12.73 | 99.9 |

[a] Theoretical iodine value for the addition of two atoms of iodine to chaulmoogric acid, $C_{17}H_{31}COOH = 90.6$; for the addition of two atoms of iodine to hydnocarpic acid, $C_{15}H_{27}COOH = 100.6$

*Preparation and description of samples.*—A sample of chaulmoogra oil was washed with three separate portions of alcohol. The alcohol took on the color of the chaulmoogra oil, and a partial solution of the two took place. The separation was effected by adding water to the mixture, when the alcohol and oil formed separate layers. The alcohol-washed oil had the properties noted in Table VIII.

TABLE VIII.—*Properties of chaulmoogra oil after washing with alcohol*

| | |
|---|---|
| Specific gravity | 0.9530 |
| Specific rotation in chloroform for sodium light | +52.11 |
| Acid value cc. 0.1 *N* base | 2.46 |
| Saponification value | 196.3 |
| Index of refraction | 1.4735 |

The alcohol extract after extraction with petroleum ether was distilled under lowered pressure until all the water and alcohol were removed and only a small residue remained; it was then dried over sulphuric acid in a vacuum desiccator. The residue is a golden yellow, viscous, almost odorless, noncrystallizable mass. It constitutes about 0.06 per cent of the original oil. It was insoluble in olive oil, but was suspended in 50 cubic centimeters of this oil, marked No. 1, and submitted to the authorities at Culion with the following directions:

Directions: 1 cubic centimeter=80 cubic centimeters chaulmoogra oil; initial dose 0.10 cubic centimeter increasing to 0.50 cubic centimeter; shake before using.

The sample used in this manner at no time caused a reaction, that is, it appeared to be physiologically inactive when given in the above doses. The petroleum ether extract of the alcohol extract was placed on the steam bath for the removal of the petroleum ether and finally dried in a vacuum desiccator. This oil,

marked No. 2, is darker than No. 3 (described later); it is solid at ordinary temperature (30° C.). It constituted about 26.2 per cent of the original oil.

Directions: Dose same as chaulmoogra.

The alcohol-washed oil was then placed in a cold room (temperature, 17° to 19° C.) for four days, where it hardened to a viscous mass. When placed in cheesecloth and hung, only a very small portion separated. It was then placed in a hand press and subjected to pressure. The fractions resulting were again subjected to fractionation by means of the press, and the hard fractions were mixed, and the soft samples that resulted were mixed. The soft oil fraction, known as No. 4, was the darkest of the three samples. It is soft at 17° C. and constitutes about 20.7 per cent of the original oil.

The hard oil fraction, submitted to Culion as No. 3, is darker than No. 2, but not so dark as No. 4. It is hard at 17° C. and constitutes about 53 per cent of the original oil. The directions for Nos. 3 and 4 were identical with the directions for No. 2.

The chemical constants of these three fractions are tabulated in Table IX.

TABLE IX.—*Constants of fractions Nos. 1, 2, and 3.*

| Sample No. | Specific gravity at 30° C. | Specific rotation in chloroform for sodium light. | Acid value in cc. 0.1 *N* base. | Saponification value. | Index of refraction. | Iodine value. | Original oil. | Remarks. |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | *P. cent.* | |
| 2 | 0.9440 | +52.35 | 17.08 | 190.2 | 1.4699 | 98.7 | 26.2 | Solid at 30° C. |
| 3 | 0.6522 | +55.03 | | 194.4 | | 100.2 | 53.0 | Solid at 17° C. |
| 4 | 0.9537 | +54.84 | | 191.3 | 1.4764 | 103.4 | 20.7 | Liquid at 17° C. |

None of the fractions showed any greater activity than the original chaulmoogra oil, that is, no more marked reactions were observed than are caused by the administration of chaulmoogra oil.

Sample 2, Table II, which was obtained by petroleum ether extraction of seeds received from Madras from H. G. Carter, economic botanist to the Botanical Survey of India, and listed as seeds of chaulmoogra, was forwarded as No. 5. Its properties place it with chaulmoogra oil. Directions: Dose same as chaulmoogra oil. The sample gave no reaction, differing in intensity from that of ordinary chaulmoogra oil when it was administered. It seemed no less active than many commercial samples used by the Public Health Service.

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TABLE X.—*Data on seeds of chaulmoogra.*

| | Grams. | Per cent. |
|---|---|---|
| Whole nuts | 10,366 | |
| Kernels | 6,372 | 61.47 |
| Shells | 3,994 | 38.53 |
| Dry kernels | 5,959 | 57.48 |
| Oil extracted with petroleum ether | 3,160 | |
| Oil based on whole nut | | 30.48 |
| Oil based on dry kernel | | 53.03 |
| Alcoholic extract | 370 | |
| Alcoholic extract based on whole nut | | 3.57 |
| Alcoholic extract based on dry kernel | | 6.20 |
| Water extract | 350 | |
| Water extract based on whole nut | | 3.37 |
| Water extract based on dry kernel | | 5.87 |

The ground petroleum ether extracted nuts were then extracted with hot absolute alcohol, and the alcohol extract was evaporated to small bulk. A large quantity of sugar (glucose) separated from the mother liquor. After the separation of the free glucose the extract was evaporated to dryness, and the residue was dissolved in water and extracted with chloroform. The chloroform was evaporated, and the residue was dissolved in water and evaporated very slowly over sulphuric acid. No crystalline product was obtained. The sample had a somewhat bitter taste. It was dissolved in a mixture of alcohol and olive oil and forwarded to Culion as No. 6.

Directions: Contents, 100 cubic centimeters; initial dose 1 cubic centimeter, to be increased later if advisable; shake before using.

In one case this sample gave a decided reaction, but no repetitions of this reaction were obtained.

One half of the material after having been extracted with chloroform was dissolved in 200 cubic centimeters of 15 per cent alcohol and forwarded as No. 7.

Directions: Initial dose 1 cubic centimeter to be increased later if advisable; shake before using.

No noticeable reaction was obtained with this fraction.

An attempt was made to isolate a crystalline product from the remaining half of the extract. A small amount of sugar only was obtained. Apparently the glucoside, originally present, has been hydrolyzed by the enzymes and moisture.

One half of the water extract obtained by treatment of the ground seeds after the alcohol treatment was dissolved in 500 cubic centimeters of 15 per cent alcohol and submitted as No. 8.

The remainder was examined for crystalline bodies without any success.

Directions: Initial dose 5 cubic centimeters, to be increased later if advisable; shake before using.

No reaction was observed when No. 8 was administered.

The ethyl esters of the acids present in chaulmoogra oil were prepared by esterification of a mixture of alcohol and chaulmoogra oil, using hydrochloric acid gas as the dehydrating agent. The excess acid was neutralized by adding dry sodium carbonate. This sample was submitted as No. 9. No observed reactions attended its administration.

Because of the reputed superiority of the crude oil over the refined oil, the two remaining samples were prepared. To determine if the greater effectiveness of the crude oil might be due to the presence of free acids, No. 10 was prepared. Two hundred grams of chaulmoogra oil were saponified, and the free acids were dissolved in a portion of the original oil. This preparation had an acid value of 11.47 cubic centimeters 0.1 *N* base.

Directions: Dose same as chaulmoogra oil.

The reactions observed were reported as no more marked than the reactions caused by chaulmoogra oil itself.

## EXPERIMENTS WITH AMYGDALIN

The other speculation, regarding the cause of the greater effectiveness of the crude oil, that it might be due to the presence of small amounts of the cyanogenetic glucoside, induced us to investigate the effect of amygdalin on leprosy. Amygdalin [15] is hydrolyzed by emulsin, crab juice, and acids, giving glucose, benzaldehyde, and hydrocyanic acid. Wöhler and Frerichs [16] state that amygdalin in small quantities is not poisonous to dogs, but when given in quantities of from 4 to 5 grams it causes sickness, and when accompanied by emulsin it is extremely poisonous, since it is hydrolyzed by the enzyme giving free hydrocyanic acid.

To determine the rapidity with which it is eliminated from the blood stream, 0.25 gram was dissolved in 1 cubic centimeter of water, and this solution was injected into the vein of the right ear of a rabbit. Four rabbits were so treated. At the end of two, ten, and twenty-four hours 0.5 cubic centimeter quantities of blood were drawn from the left ears of the rabbits, and this

[15] Abderhalden, Emil, Biochemisches Handlexikon. Julius Springer, Berlin (1911), 2, 707.

[16] *Annal. d. Chem. & Pharm.* (1848), 65, 337.

blood was tested for the presence of amygdalin by hydrolysis with hydrochloric acid and was tested for hydrocyanic acid by distilling into alkali and using ferrous sulphate paper, with the results noted in Table XI.

TABLE XI.—*Elimination of amygdalin from blood stream of rabbits.*

| Rabbit. | Results. | | |
|---|---|---|---|
| | 2 hours. | 10 hours. | 24 hours. |
| 1 | ++ | ([a]) | — |
| 2 | ++ | ([a]) | — |
| 3 | ++ | ([a]) | — |
| 4 | ++ | ([a]) | — |

++, fair test for hydrocyanic acid; —, negative for hydrocyanic acid.
[a] Questionable.

The results indicate that the amygdalin no longer exists in the blood stream after ten hours.

Tests were made with blood and blood serum from lepers and with blood from apparently healthy people by incubating the samples with a standard amygdalin solution to determine if any difference exists in their hydrolytic powers on amygdalin.

TABLE XII.—*Quantity of hydrocyanic acid liberated by the action of blood on amygdalin.*

| Kind of blood. | Quantity of amygdalin solution (1 gram in 150 cc. of water). | Quantity of 0.1 *N* silver nitrate solution used. | Hydrocyanic acid liberated in per cent of original. | Hydrocyanic acid liberated. |
|---|---|---|---|---|
| | *cc.* | *cc.* | | |
| Leper | 25 | 1.10 | 3.68 | 0.000360 |
| Blood serum from leper | 25 | 1.63 | 5.50 | 0.000540 |
| Healthy | 25 | 0.22 | 0.60 | 0.000059 |
| Do | 25 | 0.22 | 0.60 | 0.000059 |
| Do | 25 | 0.38 | 1.05 | 0.000103 |
| Do | 25 | 0.38 | 1.05 | 0.000103 |
| Do | 25 | 0.36 | 0.98 | 0.000097 |
| Do | 25 | 0.28 | 0.77 | 0.000076 |
| Do | 25 | 0.47 | 1.30 | 0.000128 |
| Do | 25 | 0.49 | 1.33 | 0.000132 |
| Do | 25 | 0.34 | 0.94 | 0.000092 |
| Do | none. | 0.38 | 1.05 | 0.000103 |
| None | 25 | 0.40 | 1.10 | 0.000108 |

While the absolute results may not be of extreme accuracy, they are comparable and indicate that leper blood may have greater hydrolytic power on amygdalin than does normal blood.

It is to be regretted that we were unable to procure more leper blood in order that this study might have been extended.

To determine the action of amygdalin on lepers, tablets weighing approximately 0.05 gram were made and submitted as No. 11.

Directions: One tablet every other day gradually increasing the size and frequency of the dose.

The Culion authorities reported no marked reactions with amygdalin, but the trial was not over a long period. It might give more favorable results under improved conditions.

## HYDNOCARPUS ANTHELMINTICA

For the purpose of further confirming the results of Power and others on their work on chaulmoogra and hydnocarpus oils, the constants of the oil from the seeds of *Hydnocarpus anthelmintica* obtained from Madras, through the kindness of H. G. Carter, and examined in the Bureau of Science, are added.

TABLE XIII.—*Constants of oils from Hydnocarpus anthelmintica seeds.*

| | Results. | |
|---|---|---|
| Specific gravity at 30° C | 0.9487 | [a] 0.9520 |
| Specific rotation in chloroform for sodium light | +49.50 | 51.0 |
| Acid value cc. 0.1 *N* base | 0.6 | 8.1 |
| Saponification value | 206.2 | 208.0 |
| Index of refraction | 1.4725 | ---------- |
| Iodine value | 90.8 | 82.5 |

[a] At 25° C. Results of Power and Barrowcliff, loc. cit.

The results are close enough to prove the identity of the seeds furnishing the two oils.

## DISCUSSION

As has been previously stated, the medicinal administration of chaulmoogra oil should be accompanied by the chemical control of the samples used. It seems plausible to think that the slowness of the changes caused by the use of chaulmoogra oil in the treatment of leprosy may be due to the small quantity of the active constituent present in the oil. If this constituent could be isolated and administered in concentrated form, more rapid cures should result, and the treament would undoubtedly be less painful.

The results of Rogers [17] with the free acids and the sodium

[17] Loc. cit.

salts make the use of these appear as promising remedies. But Rogers cautions against the assumption of a too optimistic attitude, as he regards the problem as still unsolved. On the other hand, it seems likely that antileprol and the neutral oil should be more effective than they have been found to be, if cures result from the use of the free acids and of the sodium salts. Consequently the inactivity of antileprol and of many of the commercial chaulmoogra oils should make practitioners cautious about accepting a remedy as specific for leprosy until it is proved to be such.

## SUMMARY

The constants of ten samples of chaulmoogra oil are given. A chemical examination of chaulmoogra oil is included. The use of various fractions of chaulmoogra in the treatment of leprosy is discussed, and the desirability of chemical investigation accompanying the medicinal administration is pointed out.

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## CONTENTS




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ALVIN J. COX, M. A., PH. D.
GENERAL EDITOR

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# JOURNAL OF SCIENCE

A. CHEMICAL AND GEOLOGICAL SCIENCES
AND THE INDUSTRIES

VOL. XII SEPTEMBER, 1917 No. 5

## THE COMPOSITION AND MOISTURE CONTENT OF THE SOILS IN THE TYPES OF VEGETATION AT DIFFERENT ELEVATIONS ON MOUNT MAQUILING[1]

By WILLIAM H. BROWN and ANGEL S. ARGÜELLES

*(From the College of Liberal Arts, University of the Philippines, and the Bureau of Science, Manila)*

THREE PLATES AND ONE TEXT FIGURE

In the Philippines, as in other moist tropical countries, there are frequently decided changes both in the composition and in the physical character of the vegetation even in very limited areas. One of the most remarkable examples of this is the frequency with which vegetation becomes dwarfed at comparatively low elevation. On Mount Maquiling a lofty forest occurs at elevations up to 600 meters, while at an altitude of 1,000 meters the ground is covered by elfin wood. The object of the work here reported was to determine whether or not the types of vegetation on the eastern and southeastern slopes of Mount Maquiling could be correlated with the composition and water content of the soils.

The soil of the Philippines is largely of volcanic origin. Cox[2] has published the results of a large number of analyses of soil from different parts of the Archipelago. He concluded that both the chemical and physical analyses indicated that the soil of the Islands was on the whole fertile. Cox also shows that the distribution of cultivated crops appears to be determined largely by the

[1] Received for publication June, 1917.

[2] Cox, Alvin J., Philippine soils and some of the factors which influence them, *This Journal, Sec. A* (1911), **6**, 279–330, Pls. I–XI.

character of the rainfall, certain plants being grown more extensively where there is a distinct dry season and others where the rain is more evenly distributed throughout the year. A more intensive study of the soils of Luzon has been published by Cox and Argüelles.[3]

Brown and Matthews[4] have shown that in the Philippines the present distribution of forest and grassland is due to the activity of man combined with climatic influences. Grasslands only occur where the forests have been removed. They are produced and maintained by frequent fires and so are most extensive where there is a pronounced dry season.

## MOUNT MAQUILING

Mount Maquiling is an isolated volcanic cone, situated on Luzon, midway between the eastern and western coasts, about 64 kilometers southeast of Manila, in latitude 14° 10′ east of Greenwich. It reaches an altitude of approximately 1,100 meters. The geology of the mountain, particularly of the lower slopes, has been described in considerable detail by Abella.[5]

The main crater of the volcano has apparently been extinct for a long period. The rim has been eroded until it has become a series of peaks which, except on very steep slopes, are covered with deep soil. Volcanic activity has, however, not entirely ceased, as numerous fumeroles and hot springs occur around the base and on the lower slopes.

On the eastern and southeastern sides the mountain grades into the surrounding plain at an elevation of approximately 50 meters. On the lower slopes there are layers of soft volcanic tuff. At elevations of from 50 to 100 meters these layers of tuff, which are mixed with layers of soil, may be many feet thick and are frequently near the surface. The layers near the surface are, however, usually thin, soft, and very much broken. Such a layer, about 30 centimeters thick, is frequently found about 30 centimeters below the surface, and traces of such a layer occur at elevations as great as 300 meters or more. West and Cox[6] give

[3] Cox, A. J., and Argüelles, A. S., The soils of the Island of Luzon, ibid., *Sec. A* (1914), **9**, 1–50.

[4] Brown, W. H., and Matthews, D. M., Philippine dipterocarp forests, ibid., *Sec. A* (1914), **9**, 413–561, Pls. I–XIII.

[5] Abella y Casariego, D. E., El Monte Maquilin (Filipinas) y sus actuales unanaciones volcanicas. Imprenta y Fundación de M. Tullo, Madrid (1885), 1–28, Pls. 1–2.

[6] West, A. P., and Cox, A. J., Burning tests of Philippine Portland cement raw materials, *This Journal, Sec. A* (1914), **9**, 79.

analyses of a number of samples of similar tuff. These analyses indicate that the tuff should disintegrate into a fertile soil. Where the surface layers of the tuff are shallow and much broken, they appear to have little if any effect in determining the character of the vegetation. We have seen thick surface layers only around the base, where the original vegetation has been almost entirely removed.

The climate of Mount Maquiling may be classified as monsoonal; that is, the rains depend upon rain-bearing winds, which shift their direction twice a year. This results in distinct wet and dry seasons. The northeastern monsoon strikes Luzon on its eastern coast and deposits a large part of its moisture in passing over the divide between the Pacific Ocean and Laguna de Bay; when it reaches Mount Maquiling, it is a drying wind. This monsoon results in a decided dry season from January to April. The most pronounced rainy season is from July to September during the southwest monsoon, when a large part of the rains are the result of cyclonic disturbances (typhoons).

Around the base and on the lower slopes of Mount Maquiling there is a mixture of grassland and second-growth forest. Above this there are three distinct types of original forest, which occur at successively higher levels.

## GRASS AREA

The mixture of grassland and second-growth forest at the base has been described by Brown and Matthews.[7] This region appears to have been originally covered with a tall dipterocarp forest, which is the type occurring at the next higher elevations. The original forest was removed, and the land was cultivated. In the area under consideration cultivation was abandoned, and much of the ground became covered by tall grasses, chiefly *Saccharum spontaneum* (talahib) and *Imperata exaltata* (cogon). These grasses are very inflammable when dry. They were burned at frequent intervals, the last fire occurring in 1911. The grass fires kill nearly all tree seedlings, but appear to do little if any damage to the rhizomes of the grasses. *Saccharum spontaneum* (Plate 1, fig. 1) and *Imperata exaltata* both form dense stands, the former frequently reaching a height of over 3 meters, while the latter is shorter, being rarely more than 1.5 meters in height. Mixed with the grass are areas of second-growth forest, and since 1911 much of the grassland has changed to

[7] Op. cit.

forest, as quick-growing trees readily invade the grass areas when there are no fires. The trees have a very rapid rate of growth and are small, usually reaching a height of only 10 meters or less.

Our soil samples from this altitude were taken in a grass area at an elevation of approximately 100 meters.

### DIPTEROCARP FOREST

At altitudes between 200 and 600 meters the ground is covered by a tall, dense dipterocarp forest. This is composed of three distinct stories of trees, the tallest of which reaches a height of from 35 to 40 meters (Plate I, fig. 2). The most prominent tree in it is *Parashorea plicata,* which is frequently more than a meter in diameter. The second, or middle story, is composed of medium-sized trees, which spread their leaves under the branches of those of the top story. The second story reaches a height of about 18 or 20 meters. The most prominent species is *Diplodiscus paniculatus* (balobo), which is represented by many more trees than any other species in the forest and is probably about four times as numerous as any other second-story species. The third story is composed of small trees that reach a height of about 10 meters.

The presence of the different stories is not evident on casual observation, as the specific composition of the stories is very complex and few of the trees present any striking peculiarities, while smaller trees of a higher story always occur in a lower story and between the different stories. In addition to the above stories of trees there is a ground cover composed largely of seedlings of tree species and climbing palms (rattans), but also containing numerous herbs and shrubs.

The foliage is so dense that when one walks through the forest most of the large trees are completely hidden from view. Plate II, fig. 1, shows an area from which the undergrowth and small trees have been removed. It will be seen that large trees are much more numerous than would be suspected from an examination of Plate I, fig. 2, which shows a virgin area where there are probably as many trees as in the area shown in Plate II, fig. 1.

For a fuller discussion of this forest, see an article by Brown and Matthews.[8]

The soil samples in the dipterocarp forest were obtained near the top of a ridge at an altitude of about 300 meters.

[8] Op. cit.

## MIDMOUNTAIN FOREST

The forest occurring above the dipterocarp forest is much smaller than the latter and is composed of only two stories of trees (Plate II, fig. 2). This forest extends upward to an elevation of approximately 900 meters. The soil samples considered in this paper were obtained on the top of a broad ridge at an elevation of about 730 meters. In this locality the trees of the top story reach a height of about 18 meters. The forest is much more open than the dipterocarp forest (Plate III, fig. 1). The most prominent large tree in it is *Quercus solariana* (*cataban*), while *Cratoxylon celebicum* (*guyong guyong*), which is somewhat smaller, is more numerous. The average height of the second story is about 6 or 8 meters. The most numerous species are *Oreocnide trinervis* (*malatuba*), *Neolitsia villosa,* and *Sauraunia barnsii.* The ground cover consists largely of ferns and other herbs, of which species of *Elatostema* are the most prominent. The herbs in this region require much moister conditions than those in the dipterocarp forest.

## MOSSY FOREST

The top of the mountain is in the cloud belt and is covered with an elfin wood or mossy forest. This type is composed of only one story and is characterized by having the trunks of the trees thickly covered by mosses, mosslike plants, and other epiphytes. The ground cover is composed almost entirely of herbs, among which *Strobilanthus plurifomis,* ferns, and species of *Selaginella* are the most prominent. The most striking peculiarity of the trees is a tendency to produce a large number of aërial roots, which grow to such a size as to form, as far as function goes, secondary trunks (Plate III, fig. 1). The soil samples from this forest were taken within a few meters of the top of the mountain.

From the above description it will be seen that the chief changes caused by increased altitude, which might conceivably be connected with soil conditions, are a dwarfing of the vegetation as higher elevations are reached and the occurrence in the ground cover of plants requiring moister conditions at high than at low altitudes. In order to see whether or not these changes could be connected with soil conditions, we have made a chemical and physical analysis of soil samples taken at a depth of 20 centimeters in the four different types of vegetation and have determined the water content of the soils, for different weeks

of the year, in the same locations at depths of 10, 20, and 30 centimeters.

## CHEMICAL COMPOSITION

In Table I are given chemical analyses of the soils from the different altitudes.

TABLE I.—*Chemical analyses of soils from Mount Maquiling, Laguna Province, Luzon.*

[Water-free basis, numbers give percentages.]

| | Source of soil. | | | |
|---|---|---|---|---|
| | Grassland. | Dipterocarp forest. | Mid-mountain forest. | Mossy forest. |
| Loss on ignition | 10.32 | 10.08 | 13.56 | 29.97 |
| Nitrogen ($N_2$) | 0.150 | 0.137 | 0.199 | 0.644 |
| Phosphoric anhydride ($P_2O_5$) | 0.278 | 0.106 | 0.104 | 0.112 |
| Lime (CaO) | 0.86 | 1.01 | 0.31 | 0.52 |
| Magnesia (MgO) | 0.62 | 0.61 | 0.49 | 0.79 |
| Potash ($K_2O$) | 0.294 | 0.241 | 0.189 | 0.170 |
| Soda ($Na_2O$) | 0.37 | 0.44 | 0.53 | 0.34 |
| Humus | 1.36 | 1.06 | 1.71 | 8.06 |
| Soil acidity ($CaCO_3$ equivalent) | 0.0069 | 0.0100 | 0.0094 | 0.0082 |

It will be seen that none of the soils are strikingly deficient in any important element and none can be considered as acid. The amount of nitrogen and humus is greatest in the mossy forest, where the vegetation is most dwarfed. It is to be noted that the smallest amount of nitrogen and humus is shown by the sample from the tall dipterocarp forest. The chemical analyses of the soil, as shown in Table I, do not indicate that there is any connection between the chemical composition of the soil and the dwarfing of the vegetation as higher elevations are reached.

## PHYSICAL COMPOSITION

The physical analyses of the soils from the different types of vegetation are given in Table II.

There is nothing in these analyses to indicate that all of the soils should not produce a luxuriant type of vegetation. If any distinction can be made, it seems that the soil of the mossy forest should be the best, as this is a fine sandy loam, while the soil of the dipterocarp forest and grassland is a loamy clay.

TABLE II.—*Mechanical analyses of soils from Mount Maquiling, Laguna Province, Luzon.*

[Water-free basis, numbers give percentages.]

| Classification of soil. | Diameter of particles. | Source of soil. | | | |
|---|---|---|---|---|---|
| | | Grass-land. | Dip-ter-ocarp forest. | Mid-moun-tain forest. | Mossy forest. |
| | *mm.* | | | | |
| | Over 2 | nil | nil | nil | nil |
| | 2 to 1 | 0.9 | 0.5 | 0.7 | nil |
| Coarse sand | 1.0 to 0.5 | 2.2 | 1.3 | 0.9 | 5.9 |
| Medium sand | 0.5 to 0.25 | 5.4 | 4.5 | 4.1 | 23.3 |
| Fine sand | 0.25 to 0.10 | 12.5 | 9.8 | 8.8 | 31.4 |
| Very fine sand | 0.10 to 0.05 | 10.8 | 7.8 | 12.3 | 13.2 |
| Silt | 0.05 to 0.01 | 13.6 | 13.5 | 4.9 | 11.2 |
| Very fine silt | 0.01 to 0.002 | 36.5 | 41.7 | 39.4 | 9.4 |
| Clay | Less than 0.002 | 19.0 | 21.4 | 29.6 | 5.6 |

## MOISTURE CONTENT

In Tables III to VI is shown the percentage of moisture in the soil at the different altitudes.

TABLE III.—*Percentage of soil moisture in grassland (altitude 100 meters) at base of Mount Maquiling, Laguna Province, Luzon.*

| Date. | Depth in centimeters. 10. | 20. | 30. | Date. | Depth in centimeters. 10. | 20. | 30. |
|---|---|---|---|---|---|---|---|
| 1912. | | | | 1913—Cont. | | | |
| December 6 | 30.3 | 34.5 | 33.6 | May 2 | 27.6 | 27.5 | 27.8 |
| 13 | 34.1 | 34.7 | 35.5 | 9 | 27.0 | 26.8 | 27.1 |
| 20 | 35.6 | 34.6 | 35.3 | 16 | 33.8 | 28.7 | 30.3 |
| 27 | 36.9 | 35.7 | 35.6 | 23 | 34.3 | 34.8 | 32.8 |
| 1913. | | | | 30 | 33.3 | 32.7 | 33.1 |
| January 3 | 38.5 | 39.4 | 39.1 | June 6 | 30.8 | 30.3 | 31.9 |
| 10 | 38.7 | 35.5 | 37.6 | 20 | 33.2 | 38.8 | 29.9 |
| 17 | 34.1 | 38.1 | 39.8 | July 18 | 40.9 | 33.9 | 35.1 |
| 24 | 37.6 | 36.4 | 37.6 | 25 | 33.9 | 35.7 | 36.0 |
| 31 | 34.2 | 33.4 | 33.3 | August 1 | 35.8 | 34.8 | 35.7 |
| February 7 | 30.3 | 30.4 | 31.5 | 8 | 36.4 | 36.1 | 35.6 |
| 14 | 33.2 | 34.6 | 35.5 | 15 | 37.7 | 33.5 | 34.7 |
| 21 | 35.8 | 33.6 | 33.0 | 22 | 38.3 | 35.1 | 36.8 |
| 28 | 35.6 | 34.6 | 33.6 | 29 | 39.7 | 36.8 | 35.2 |
| March 7 | 35.6 | 34.8 | 38.5 | September 5 | 38.9 | 39.2 | 40.1 |
| 14 | 31.2 | 32.4 | 33.8 | 26 | 38.7 | 35.8 | 40.6 |
| 21 | 27.2 | 25.6 | 28.3 | October 3 | 36.6 | 37.8 | 36.9 |
| 28 | 25.8 | 23.8 | 28.3 | 24 | 35.1 | 34.3 | 33.4 |
| April 4 | 25.0 | 29.3 | 28.6 | November 7 | 33.6 | 32.7 | 31.7 |
| 11 | 24.1 | 24.2 | 27.7 | 14 | 31.8 | 35.4 | 34.3 |
| 18 | 29.2 | 26.5 | 27.1 | 21 | 41.3 | 38.7 | 42.6 |
| 25 | 30.5 | 30.6 | 33.4 | 28 | 39.1 | 37.1 | 38.1 |

One of the most striking peculiarities about these tables is the similarity in the amount of moisture in any given soil at different depths. This is apparently due to the fact that the dense covering of the vegetation prevents the surface soil from drying out at a much more rapid rate than the deeper layers.

The average percentage by months of the moisture in the soil at a depth of 20 centimeters, at elevations of 90, 350, and 725 meters, is shown graphically in fig. 1.

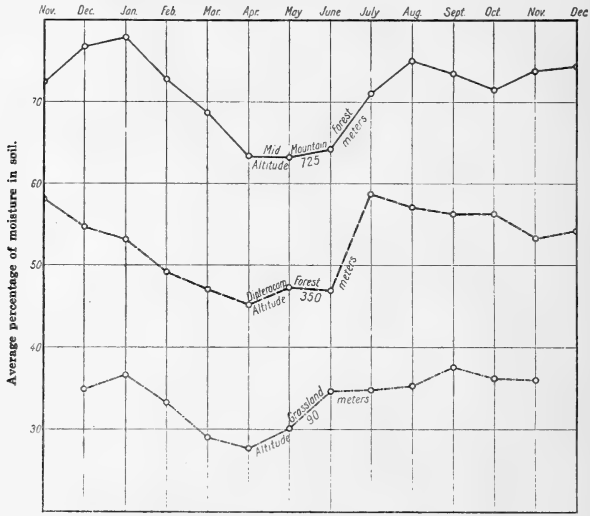


FIG. 1. Average percentage, by months, of moisture in the soil at a depth of 20 centimeters at different elevations on Mount Maquiling.

The lowest moisture content is shown by the grassland at the base of Mount Maquiling (Table III). Here, however, the growth of trees is much more rapid than at any of the higher elevations. This is very probably not due at all to soil conditions, but to the greater illumination of the individual trees and the rapid rate of growth characteristic of the second-growth species.

At a depth of 10 centimeters the greatest variation of water content is from 41.3 per cent on November 21 to 24.1 per cent on April 11. The soil samples taken in different places in a very limited area on the same day would, of course, show varia-

tions in water content. Some of the variations seen in Table III are undoubtedly due to the selection of individual samples and are not connected with any change in the water content of the soil as a whole. It is probable that this source of error is responsible for the extreme variations noted in the water content given in Table III. The soil at a depth of 10 centimeters gives an average water content for November of 38 per cent and for April of 27 per cent. These figures would probably represent the extreme variations for the region as a whole more accurately than the highest and lowest figure shown in Table III. The figures for April show that even in the dry season the soil contains considerable moisture. The lower moisture content combined with the dry atmospheric conditions at this season are, however, sufficient to affect the plants very adversely. Many of the second-growth tree species loose their leaves completely for longer or shorter periods, and all of them show a much lower rate of growth during the dry season than at other times of the year.

TABLE IV.—*Percentage of moisture in soil in dipterocarp forest (altitude 300 meters) on Mount Maquiling, Laguna Province.*

| Date. | Depth in centimeters. | | | Date. | Depth in centimeters. | | |
|---|---|---|---|---|---|---|---|
| | 10. | 20. | 30. | | 10. | 20. | 30. |
| 1912. | | | | 1913—Cont. | | | |
| November 15 | 57.4 | 57.1 | 56.6 | May 2 | 44.2 | 46.2 | 48.1 |
| 22 | 57.2 | 59.5 | 56.5 | 9 | 45.1 | 42.9 | 42.4 |
| 29 | 57.2 | 57.8 | 58.6 | 16 | 50.7 | 49.4 | 51.0 |
| December 6 | 55.2 | 57.8 | 56.5 | 30 | 51.4 | 50.8 | 55.4 |
| 13 | 53.1 | 54.4 | 52.3 | June 6 | 46.1 | 45.4 | 46.6 |
| 20 | 54.2 | 52.4 | 56.2 | 13 | 42.0 | 43.5 | 44.7 |
| 27 | 60.4 | 54.6 | 54.5 | 20 | 54.8 | 51.7 | 54.4 |
| 1913. | | | | July 18 | 53.2 | 59.8 | 57.9 |
| January 3 | 55.5 | 54.7 | 57.0 | 25 | 56.1 | 57.3 | 59.4 |
| 10 | 53.8 | 52.2 | 54.2 | August 1 | 52.4 | 52.9 | 50.0 |
| 17 | 51.2 | 47.2 | 54.9 | 8 | 54.8 | 56.2 | 55.1 |
| 24 | 53.6 | 57.4 | 60.0 | 15 | 53.0 | 57.8 | 60.0 |
| 31 | 54.6 | 54.4 | 56.3 | 22 | 58.1 | 57.2 | 55.8 |
| February 7 | 47.1 | 45.8 | 51.7 | 29 | 64.5 | 61.2 | 58.8 |
| 14 | 47.6 | 50.5 | 53.5 | September 5 | 55.4 | 53.9 | 51.2 |
| 21 | 55.6 | 52.5 | 48.0 | 12 | 54.8 | 53.8 | 55.1 |
| 28 | 44.9 | 48.1 | 47.1 | 19 | 57.0 | 61.2 | 59.4 |
| March 7 | 47.5 | 52.4 | 51.5 | October 3 | 55.4 | 57.7 | 56.1 |
| 14 | 45.9 | 46.7 | 47.9 | 24 | 56.1 | 54.8 | 54.4 |
| 21 | 39.0 | 45.0 | 50.3 | November 7 | 55.2 | 51.2 | 52.1 |
| 28 | 40.6 | 44.1 | 48.8 | 14 | 55.1 | 54.6 | 54.2 |
| April 4 | 42.4 | 41.4 | 44.5 | 21 | 58.4 | 52.0 | 47.6 |
| 11 | 41.3 | 42.6 | 44.5 | 28 | 55.2 | 55.3 | 55.1 |
| 18 | 52.1 | 49.4 | 49.8 | December 12 | 57.2 | 55.4 | 54.3 |
| 25 | 42.1 | 47.6 | 44.8 | 19 | 59.1 | 59.1 | 59.4 |
| | | | | 26 | 51.2 | 48.1 | 50.8 |

The soil of the dipterocarp forest contains considerably more water than that of the grassland. The greatest variation in moisture content at a depth of 10 centimeters is from 59.1 per cent on December 19 to 39 per cent on March 21. The latter figure appears to be high for a minimum water content at this depth, but during the dry season the effects of drought on the dipterocarp forest are very evident. The foliage is much less dense than at other seasons, while *Parastaca plicata* (*bagtican lauan*), the dominant tree, shows a greatly diminished rate of growth.[9] The effect of drought in the dipterocarp forest is, however, not so marked as in the grassland.

The percentages of moisture shown in Table V for the midmountain forest are considerably greater than those for the dipterocarp forest, and the variation is relatively less.

TABLE V.—*Percentage of moisture in soil in midmountain forest (altitude 730 meters) on Mount Maquiling, Laguna Province, Luzon.*

| Date. | Depth in centimeters. | | | Date. | Depth in centimeters. | | |
|---|---|---|---|---|---|---|---|
| | 10. | 20. | 30. | | 10. | 20. | 30. |
| 1912. | | | | 1913—Cont. | | | |
| November 16 | 82.9 | 73.7 | 76.8 | May 3 | 59.1 | 58.8 | 62.0 |
| 23 | 68.2 | 71.2 | 70.3 | 10 | 61.7 | 63.1 | 62.9 |
| 30 | 73.5 | 72.3 | 77.7 | 17 | 59.2 | 67.8 | 65.2 |
| December 7 | 75.0 | 78.1 | 77.8 | 31 | ------ | 62.9 | 55.2 |
| 14 | 78.0 | 76.2 | 74.5 | June 7 | 64.9 | 63.6 | 65.7 |
| 21 | 72.7 | 74.5 | 73.5 | 14 | 58.9 | 60.6 | 62.0 |
| 28 | 79.0 | 78.1 | 76.8 | 21 | 69.1 | 68.3 | 70.1 |
| 1913. | | | | July 19 | 82.9 | ------ | 80.1 |
| | | | | 26 | 70.7 | 71.0 | 78.7 |
| January 11 | 77.2 | 80.1 | ------ | August 2 | 71.9 | 74.5 | 73.4 |
| 18 | ------ | 75.6 | 77.5 | 23 | 70.8 | 77.6 | 70.5 |
| 25 | 76.8 | ------ | 86.2 | 30 | 67.8 | 72.7 | 71.7 |
| February 1 | 70.2 | 73.5 | 74.7 | September 6 | ------ | 74.6 | 69.3 |
| 8 | 69.1 | 72.8 | 73.5 | 20 | 68.2 | 74.9 | 71.3 |
| 15 | 70.5 | 74.7 | 76.4 | 27 | 73.1 | 70.7 | 73.8 |
| 22 | 73.7 | 69.7 | 72.0 | October 4 | 74.9 | 71.3 | 72.6 |
| March 1 | 74.6 | 73.1 | 75.6 | 25 | 65.8 | 71.4 | 78.1 |
| 8 | 70.1 | 70.7 | 74.5 | November 1 | 64.3 | 64.6 | 66.9 |
| 15 | 57.2 | 65.1 | 66.4 | 8 | 74.9 | 80.4 | 82.3 |
| 22 | 62.4 | 65.9 | 68.8 | 29 | 80.9 | 76.2 | 74.1 |
| April 5 | 57.8 | 55.2 | 60.1 | December 6 | 73.1 | 77.3 | 83.2 |
| 12 | ------ | 66.2 | 66.5 | 13 | 68.1 | 71.1 | 74.0 |
| 26 | 64.4 | 68.8 | 69.5 | | | | |

In this region there were no marked effects of droughts during the dry season except on the epiphitic vegetation. The percentage of moisture in the soil is very high, being between 70 and 80

[9] Brown and Matthews, op. cit.

per cent for a large portion of the year. There is, however, no indication that this amount is excessive, as the soil is well drained.

TABLE VI.— *Percentage of moisture in soil in mossy forest (altitude 1,070 meters) at top of Mount Maquiling, Laguna Province, Luzon.*

| Date. | Depth in centimeters. | | |
|---|---|---|---|
| | 10. | 20. | 30. |
| 1912. | | | |
| November 16 | 258.1 | 190.5 | 246.7 |
| 23 | 251.5 | 167.5 | 121.1 |
| 30 | 305.0 | 312.4 | 129.5 |
| December 7 | 275.9 | 258.2 | 123.2 |
| 14 | 291.0 | 188.1 | 180.5 |
| 21 | 234.5 | 352.8 | 232.0 |
| 1913. | | | |
| January 11 | 245.0 | 268.2 | 273.0 |
| 18 | 178.6 | 149.5 | 362.3 |
| February 1 | 130.5 | 234.3 | 305.8 |
| 8 | 211.1 | 225.2 | 289.0 |
| 15 | 250.5 | 188.0 | 206.0 |
| 22 | | 320.2 | 319.9 |
| March 1 | 281.8 | 256.0 | 255.5 |
| 8 | 257.2 | 198.8 | 198.6 |
| 15 | 221.2 | 264.9 | 232.1 |
| 22 | 203.6 | 221.8 | 257.2 |
| 29 | 306.3 | 114.6 | |
| April 19 | 167.4 | 88.2 | 75.1 |
| 26 | 176.5 | 152.0 | 139.2 |
| 1913—Cont. | | | |
| May 10 | 226.4 | 136.8 | 122.0 |
| 17 | 303.9 | 214.5 | 173.6 |
| 24 | 224.3 | 185.4 | 173.6 |
| 31 | 260.2 | 246.7 | 251.8 |
| June 7 | 159.4 | 161.7 | 162.4 |
| 14 | 209.8 | 226.0 | 206.0 |
| 21 | 212.7 | 171.0 | |
| July 19 | | 137.2 | 255.0 |
| August 2 | 237.7 | 211.8 | 231.8 |
| 9 | 273.8 | 207.6 | |
| 16 | | 104.2 | 197.7 |
| 23 | 200.1 | 146.8 | 141.2 |
| 30 | 218.3 | 199.7 | 142.8 |
| September 27 | 238.0 | 257.1 | |
| October 4 | 218.8 | | 173.1 |
| 18 | 148.1 | 164.2 | 256.2 |
| 25 | 159.9 | 305.5 | 247.9 |
| November 8 | 185.7 | 186.1 | 302.0 |
| 22 | 154.2 | 263.2 | 301.2 |
| 29 | 247.3 | 203.6 | 256.5 |
| December 6 | 165.3 | 204.8 | 272.1 |
| 13 | 134.6 | 222.1 | |

The moisture content of the soil in the mossy forest (Table VI) is extremely high. There is only one week when the determinations show less than 100 per cent of moisture, and on this occasion this is true of only two of the three depths. Equally as striking as the high moisture content is the variation from week to week and at different depths on the same week. The different depths frequently show a variation of more than 100 per cent on the same day. The high moisture content is apparently connected with the large amount of organic matter found in this soil. The amount of organic matter apparently varies greatly in different situations, and the variations in the water content, shown in Table VI, are probably due more to the places in which the samples were taken than to any weekly change in the moisture content of the soil as a whole.

The high moisture content shown by the soil in the mossy and the midmountain forests undoubtedly accounts for the fact

that the ground covering is composed of plants requiring more moisture than those found in the dipterocarp forest.

It does not seem probable, however, that the dwarfing of the vegetation is connected with this high water content. The great amount of water in the soil of the mossy forest is not due to heavy rains that would cause the soil to become leached out, as the rainfall here is about the same as it is in the place where the soil samples were taken in the dipterocarp forest and is considerably less than in the midmountain forest and in a large proportion of the dipterocarp forest. The soil of the mossy forest is, moreover, well drained, so that it must be well aërated, and it has a springy consistency. The figures in Table I show less acidity in the soil of the mossy forest than in that of the dipterocarp forest. There seems, therefore, to be no reason for considering the high moisture content of the soil as harmful. The moisture content of the soil of the midmountain forest would certainly not seem to be high enough to be deleterious to the vegetation. The fact that the trees in this situation are much smaller than those in the dipterocarp forest is probably due to the same factors that have resulted in the stunted vegetation on the top of the mountain, the difference being that these factors are more pronounced at the top.

The above discussion indicates that the moisture contents of the soil should be as favorable at high as at low altitudes and so cannot be connected with the dwarfing of the vegetation as higher altitudes are reached.

## SUMMARY

The natural vegetation of Mount Maquiling becomes more and more dwarfed as higher elevations are reached. There does not appear to be anything in the physical or mechanical composition of the soil or its moisture content which would account for this fact.

The character of the plants in the ground cover varies according to the amount of moisture in the soil at different altitudes.

# ILLUSTRATIONS

## Plate I



## Plate II



## Plate III



### TEXT FIGURE

Fig. 1. Saccharum spontaneum on Mount Maquiling; altitude, 90 meters.

Fig. 2. Dipterocarp forest, Mount Maquiling; elevation, 500 meters.

PLATE I.

Fig. 1. Dipterocarp forest with undergrowth and small trees removed, Mount Maquiling; elevation, 300 meters.

Fig. 2. Trail in midmountain forest, Mount Maquiling; elevation, 740 meters.

PLATE II.

Fig. 1. Midmountain forest, Mount Maquiling; elevation, 730 meters.

Fig. 2. Aërial roots of a tree in the mossy forest, Mount Maquiling.

PLATE III.

# A COMPARISON OF LINSEED OIL AND LUMBANG OILS AS PAINT VEHICLES [1]

By R. H. AGUILAR

*(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila)*

ONE PLATE AND ONE TEXT FIGURE

Because of its general adaptability to different kinds of paints, linseed oil has not been supplanted [2] on a commercial scale by any other oil. The lumbang oils are possible substitutes for linseed oil, and they have been much studied,[3] but little has been reported concerning their behavior with different pigments or the quality of the resulting paints. It is, therefore, hoped that the following preliminary series of comparative tests on the properties of linseed, lumbang bato, and lumbang banucalag oils may be of interest.

Lumbang bato (*Aleurites moluccana*), a large tree belonging to the family Euphorbiaceæ, is common and widely distributed in the Philippines, occurring in most islands and provinces. It occurs both as a native and as a semicultivated tree and is locally abundant. The species is one of very wide geographic distribution, extending from India through Malaya to Polynesia. It is commonly known as the candlenut tree, but has numerous local names in the various countries where it occurs. In Hawaii it is known as *kukui*.

According to Richmond and Rosario [4] the seed yields from 60 to 65 per cent oil by extraction with carbon bisulphide, ether, or chloroform and 55 per cent by hydraulic expression at 500 kilograms per square centimeter. In the present work the yield of oil was 44 per cent (calculated on the weight of the kernels) by hydraulic expression at 310 kilograms per square centimeter.

[1] Received for publication July, 1917.

[2] Gardner, H. A., Paint Technology and Tests. McGraw-Hill Book Co., New York (1911), 2.

[3] Wilcox, E. V., and Thomson, A. R., *Bull. Hawaii Agr. Exp. Sta.* (1913), 39. Brill, H. C., and Agcaoili, F., *This Journal, Sec. A* (1915), 10, 105–119.

[4] Richmond, C. F., and Rosario, M. V., ibid., *Sec. A* (1907), 2, 441.

Lumbang banucalag (*Aleurites trisperma*) is confined to the Philippine Islands. Though of wide geographic distribution in the Archipelago, extending from central Luzon to Mindanao, it is less common and much more local than is lumbang bato. The oil is darker colored and more viscous than lumbang bato oil. It is commonly supposed to cause skin eruptions on contact, but I have seen no foundation for this belief. I have handled the oil constantly in this work, but have suffered no inconvenience. The yield, calculated on the kernel weight, is about 43 per cent by hydraulic expression at 310 kilograms per square centimeter.

Brill and Agcaoili [5] found that the lumbang oils are comparable with linseed oil in drying quality of film and percentage change in weight when drying; also that they can be used as substitutes for tung, or Chinese wood, oil, the product of allied species of the same genus, *Aleurites fordii* and *Aleurites cordata*.

## EXPERIMENTAL PART

The oils used in this series of tests have the constants noted in Table I.

TABLE I.—*Oil constants.*[a]

| | Raw linseed oil. | Fresh lumbang. | |
|---|---|---|---|
| | | Bato. | Banucalag. |
| Specific gravity at 15° C | 0.9345 | 0.9252 | 0.9368 |
| Saponification value | 189.40 | 192.95 | 197.74 |
| Iodine value | 183.96 | 150.36 | 145.25 |
| Acid value cc. 0.1 $N$ KOH | 0.50 | 1.05 | 8.70 |

[a] Analyzed by F. Agcaoili, chemist, Bureau of Science.

All the tests included in this preliminary work have been carried on under ordinary Philippine laboratory conditions, that is to say, in diffused daylight, at a temperature of from 28° to 30° C., and at a relative humidity of about 75 per cent.

*Drying test.*—The drying tests were made in the usual way by spreading a small amount of oil to uniform thickness on glass plates, each 6.35 by 8.89 centimeters (2.5 by 3.5 inches) in size. The oil films were placed in a glass case and were exposed to a dry atmosphere obtained by passing a slow current of air through sulphuric acid. The changes in weight and appearance are shown in Table II and in fig. 1.

[5] Op. cit.

TABLE II.—*Comparative drying tests with linseed and lumbang oils.*[a]

| No. of curve. | Oils used. | Maximum increase in weight. | Day when maximum increase in weight was attained. | Condition of film. |
|---|---|---|---|---|
| | | *Per cent.* | | |
| 1 | Linseed, boiled commercial sample. | 13.85 | 1 | Perfectly dry, clear, and firm in one day. |
| 2 | Linseed, raw, of the best quality | 12.13 | 4 | Dry, clear, and firm between the fourth and the fifth day. |
| 3 | Lumbang bato, bottled six months. | 11.20 | 2 | Dry, clear, and firm between the second and the third day, tacky at the end of twenty days. |
| 4 | Lumbang bato, fresh | 11.03 | 4 | Dry between the fourth and the sixth day. |
| 5 | Lumbang banucalag, boiled | 8.30 | 2 | Dry and firm in two days. |
| 6 | Lumbang banucalag, fresh | 8.92 | 4 | Dry in four days, but slightly opaque. |

[a] Average weight of oil taken was 0.1415 gram.

The oil films were dry and firm about the time the maximum increase in weights was attained.

Fig. 1 shows the similarity in the behavior of the three oils. The boiled and the aged oils dry much more rapidly than the fresh oils, and the curves of weight increase are almost straight lines from the origin to the maximum point. On the other hand, the fresh oils dry very slowly the first day, then more rapidly, until the maximum increase in weight is attained.

Redman and others[6] give 11.7 per cent as the maximum increase in weight for linseed oil at the end of the sixth day and 10.5 per cent for tung oil between the eighth and the ninth day. Lippert[7] gives 12.4 per cent as the maximum increase in weight for linseed oil. The lumbang oils are, therefore, similar in this respect to linseed and Chinese tung oil.

*Paint films.*—The following methods for the preparation of paint films have been tested in the laboratory:

1. The mercury method consists in allowing a paint to spread on top of mercury and later removing the dried paint film by lifting it off the liquid metal. Films obtained in this manner

[6] Redman, L. V., Weith, A. J., Brock, F. P., *Journ. Ind. & Eng. Chem.* (1913), 5, 630.

[7] Lippert, W., *Zeitschr. f. angew. Chem.* (1898), 412.

are not uniform; they become thicker in the center than at the edges because of surface tension.

2. The amalgam method consists in painting over a piece of tin plate.[8] After the paint is dry, it is scratched at a few points and drops of mercury are placed on the scratches. The mercury amalgamates with the tin, and the paint film can be lifted off the semiliquid amalgam. The quantity of tin and mercury needed, the necessity for using only unrusted tin plate, and the time required to remove the film from the tin militate against the usefulness of this method.

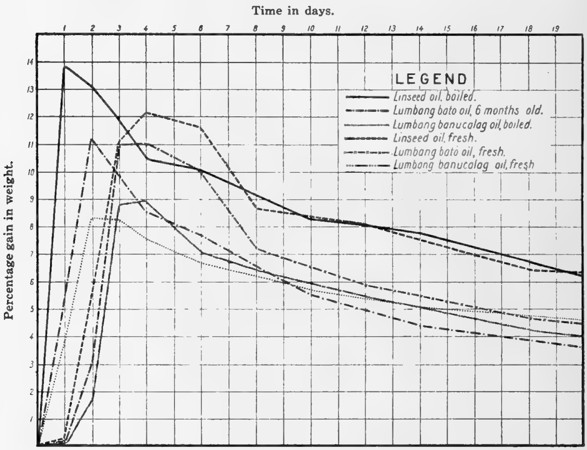


FIG. 1. Comparative drying tests for linseed, lumbang bato, and lumbang banucalag oils.

3. Lipowitz or Wood's metal can be also used. The metal is coated with the paint under examination. After the paint is dry, the metal is put on a smooth plate and gently warmed. At a temperature below its melting point (60°C.) the metal softens sufficiently to allow the stripping of the paint. Satisfactory paint films can be made in this way. This process is not well adapted to laboratory work because of the large amount of expensive alloy required and the care necessary in removing a film.

[8] Emsmann, D. H., in Brannt, W. T., Varnishes, Lacquers, Printing Inks and Sealing Waxes. H. C. Baird Co., Phila. (1893), 321.

The most satisfactory results, however, were obtained by painting over paper of fair quality, sized with some inert substance from which paint could readily be removed by soaking in warm water. Among the substances tried were library paste, agar-agar, sugar sirup, and glue. Of these, the use of paste or agar resulted in a shriveled film of low tensile strength. The use of sugar sirup [9] was satisfactory, but since the glue method, as described by Gardner, [10] was simpler and gave more uniform results, the latter was adopted for this work. The method of procedure was as follows: The paint was applied to the sized paper and allowed to dry. It was then removed by immersion in water at 40°C., washed off with fresh water to remove the glue, hung on a glass rod to dry, and placed in a suitable container to prevent the accumulation of dust and insects.

*Tensile strength and elasticity.*—In testing the paint films, a modified Gardner-de Horvath [11] film-testing machine was employed. The apparatus is shown on Plate I.

The pressure was measured by means of a mercury manometer. This was made self-registering by placing inside the manometer tube an indicator, which remained at the highest point reached by the mercury column. The stretch was recorded by means of an aluminium rod resting on the center of the film. This rod was in turn fastened to the short arm of a lever and so delicately counterpoised that it exerted no appreciable pressure, yet rose and fell with any movement of the film. As the long, or pointer, arm of the lever was ten times as long as the short arm, it is obvious that any movement of the film was transmitted tenfold to the pointer arm and could thus be estimated with a certain degree of accuracy.

To study the behavior of oil films,[12] precipitated silica passing through a 200-mesh sieve was incorporated with the oil in the proportion of 15 per cent silica by weight. The films were made of three coats of 2.5 grams of paint each, applied to 400 square centimeters of sized paper.

Table III shows the effect of age upon the strength of films made from mixtures of linseed oil with lumbang bato oil in different proportions.

[9] Labordere, P., and Anstett, F., *Chem Eng.* (1913), 17, 1.

[10] Op. cit., p. 71.

[11] Gardner, op. cit., p. 79.

[12] Gardner, op. cit., p. 31.

TABLE III.—*Effect of age upon the strength of oil-silica films.*

| Oil in mixture. | Per cent. | Breaking strength of oil-silica films in terms of centimeters of mercury, after— | | Stretches in centimeters, after— | |
|---|---|---|---|---|---|
| | | 7 days. | 60 days. | 7 days. | 60 days. |
| Linseed | 100 | 20.0 | 12.5 | 0.23 | 0.39 |
| Do | 75 | 16.4 | 8.9 | 0.25 | 0.45 |
| Lumbang | 25 | | | | |
| Linseed | 50 | 11.8 | 6.3 | 0.26 | 0.56 |
| Lumbang | 50 | | | | |
| Linseed | 25 | 10.0 | 4.2 | 0.23 | 0.54 |
| Lumbang | 75 | | | | |
| Do | 100 | 9.4 | 2.5 | 0.22 | 0.66 |

The films after sixty days were tacky and soft and of greatly reduced tensile strength.

To study the effect of age upon the strength of paint films prepared from active pigments, red lead was employed. The paints were prepared by incorporating 40 grams of red lead with 25 grams of oil, and the films were the same in weight as the oil-silica films previously described. Table IV shows the relation between the increase of strength and the age of the paint films.

TABLE IV.—*Tensile strength of red lead paint films.*

| Oils used. | Per cent. | Breaking strength in terms of centimeters of mercury. | | | | | Stretches in centimeters. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Age of film in days. | | | | | Age of film in days. | | | | |
| | | 7. | 40. | 60. | 90. | 120. | 7. | 40. | 60. | 90. | 120. |
| Linseed | 100 | 18.9 | 32.4 | 35.4 | 37.5 | 34.5 | 0.25 | 0.24 | 0.22 | 0.18 | 0.18 |
| Do | 50 | 16.1 | 23.6 | 27.2 | 28.6 | 27.1 | 0.24 | 0.23 | 0.20 | 0.19 | 0.22 |
| Lumbang bato | 50 | | | | | | | | | | |
| Do | 100 | 10.7 | 16.8 | 18.3 | 22.0 | 20.9 | 0.27 | 0.26 | 0.24 | 0.26 | 0.24 |

Table IV shows that the paint films attained their maximum strength between the third and the fourth month and that then a gradual decrease followed.

Further tests were conducted to compare the paint properties of lumbang banucalag with those of linseed oil and lumbang bato oil. Twenty-five grams of lumbang banucalag oil were mixed with 40 grams of red lead; the mixture became thick and pasty in fifteen minutes, a property by means of which it can be differentiated from lumbang bato, because the latter, very much like

linseed oil, does not show this phenomenon. The paint made with lumbang banucalag oil and red lead, painted on a smooth surface, did not dry in twelve days, probably because a very thin layer of the exposed surface dried in a very short time, thus preventing the action of the atmosphere upon the underlying paint. This property makes banucalag undesirable as a paint vehicle when used alone. However, by mixing 1 part of lumbang banucalag with from 1 to 3 parts of lumbang bato, a quick-drying and altogether satisfactory paint is obtained.

Table V shows the variation in the tensile strength of paint films made from mixtures of lumbang oils.

TABLE V.—*Tensile strength of red lead paint films.*

| No. | Oils used. | Per cent. | Breaking strength in terms of centimeters of mercury, after— | | | Stretches in centimeters, after— | | | General remarks. |
|---|---|---|---|---|---|---|---|---|---|
| | | | 10 days. | 30 days. | 60 days. | 10 days. | 30 days. | 60 days. | |
| 1 | Linseed | 100 | 26.3 | 34.0 | 38.0 | 0.27 | 0.26 | 0.29 | Film was dry in 36 hours. Appearance good. |
| 2 | Lumbang bato | 100 | 10.8 | 17.4 | 20.5 | 0.25 | 0.28 | 0.29 | Film was dry in 48 hours. Appearance good. |
| 3 | Lumbang bato<br>Lumbang banucalag | 90<br>10 | 10.2 | 15.7 | 15.5 | 0.25 | 0.24 | 0.24 | Do. |
| 4 | Lumbang bato<br>Lumbang banucalag | 75<br>25 | 12.4 | 17.6 | 17.1 | 0.32 | 0.31 | 0.26 | Film was dry in 24 hours. Appearance good. |
| 5 | Lumbang bato<br>Lumbang banucalag | 50<br>50 | 12.4 | 18.0 | 18.4 | 0.30 | 0.35 | 0.33 | Do. |
| 6 | Lumbang bato<br>Lumbang banucalag | 25<br>75 | 16.1 | 20.2 | 21.2 | 0.25 | 0.22 | 0.21 | Film was not dry in 6 days. The surface was dull. Paint dried into a paste in the container in a short time. |
| 7 | Lumbang bato<br>Lumbang banucalag | 10<br>90 | 14.2 | 22.3 | 22.4 | 0.24 | 0.27 | 0.25 | Film was not dry in 9 days. The surface was also dull. Paint dried into a paste in the container in a short time. |

The above results indicate that the mixtures of lumbang oils attain their maximum strength more quickly than either linseed or lumbang bato. Judging from the general behavior and appearance of the paints, mixtures 4 and 5, that is, mixtures with lumbang banucalag containing 50 to 75 per cent lumbang bato,

will be the most desirable for a red lead paint. With these mixtures, the resulting paint does not set as in the case of linseed [13] or lumbang bato oils; it does not dry into a paste in the container as in the case of mixtures 6 and 7; and a better paint is obtained than can be secured with linseed or lumbang bato oils alone.

*Moisture-excluding property.*—To determine the moisture-excluding property of films,[14] pieces of suitable size and shape were fastened with Canada balsam over the mouths of 200 cubic centimeter bottles containing drying agents. One set of bottles was half filled with concentrated sulphuric acid, another set with calcium chloride. The test pieces were cut from the same films as those whose tensile strength was recorded in Table IV. The moisture-excluding property of linseed and lumbang oils as determined by the increase in weight of the bottles of drying agent is shown in Table VI.

TABLE VI.—*Moisture experiment.*

[Numbers express percentage gain in weight. The calculations were based on the original weights of concentrated sulphuric acid and calcium chloride.]

| Oils used. | Per cent. | Absorbent. | Number of days. | | |
|---|---|---|---|---|---|
| | | | 5. | 10. | 40. |
| Linseed | 100 | Concentracted $H_2SO_4$ | 0.24 | 0.45 | 1.67 |
| Do | 50 | do | 0.37 | 0.69 | 2.53 |
| Lumbang | 50 | | | | |
| Do | 100 | do | 0.42 | 0.81 | 3.03 |
| Linseed | 100 | $CaCl_2$ | 1.07 | 2.00 | 6.98 |
| Do | 50 | do | 1.14 | 2.15 | 7.52 |
| Lumbang | 50 | | | | |
| Do | 100 | do | 1.18 | 2.18 | 7.76 |

Table VI shows that the moisture-excluding property of lumbang bato red lead paint films are not as high as those of linseed oil red lead paint films. The moisture absorption with calcium chloride was relatively higher than with sulphuric acid.

Similar tests were conducted with the films made from mixtures of lumbang bato and lumbang banucalag oils whose strength was shown in Table V. In this test 25 cubic centimeter bottles half filled with concentrated sulphuric acid were used. The results obtained are shown in Table VII.

[13] Cf. Holley, C. D., Analysis of Paint and Varnish Products. John Wiley and Sons, New York (1912), p. 222.

[14] Gardner, op. cit., p. 83.

TABLE VII.—*Moisture experiment.*

[Numbers express percentage gain in weight.]

| No. | Oils used. | Per cent. | Number of days. | | | |
|---|---|---|---|---|---|---|
| | | | 6. | 12. | 32. | 60. |
| 1 | Linseed | 100 | 0.05 | 0.10 | 0.43 | 0.80 |
| 2 | Lumbang bato | 100 | 0.05 | 0.13 | 0.54 | 1.04 |
| 3 | Lumbang bato<br>Lumbang banucalag | 90<br>10 | 0.07 | 0.16 | 0.53 | 1.00 |
| 4 | Lumbang bato<br>Lumbang banucalag | 75<br>25 | 0.06 | 0.15 | 0.52 | 1.00 |
| 5 | Lumbang bato<br>Lumbang banucalag | 50<br>50 | 0.06 | 0.13 | 0.49 | 0.90 |
| 6 | Lumbang bato<br>Lumbang banucalag | 25<br>75 | 0.04 | 0.13 | 0.40 | 0.83 |
| 7 | Lumbang bato<br>Lumbang banucalag | 10<br>90 | 0.04 | 0.09 | 0.35 | 0.69 |

The above results indicate that the moisture-excluding properties of mixtures 6 and 7 are higher than those of 4 and 5. However, taking into consideration the behavior and the general appearance of the paint films and the fact that mixtures 4 and 5 exclude moisture almost as well as linseed oil, I am inclined to recommend them as paint vehicles.

## SUMMARY AND CONCLUSIONS

The drying properties of lumbang bato and lumbang banucalag oils are comparable with those of linseed oil.

Lumbang bato oil is very similar to linseed oil in its properties as a paint vehicle, and like linseed has certain disadvantages for use in red lead paints.

Lumbang banucalag oil cannot be used as a paint vehicle, especially with red lead; it dries into a paste. This is also true with lumbang bato containing 75 and 90 per cent lumbang banucalag (mixtures 6 and 7, Table V).

Lumbang banucalag containing between 50 and 75 per cent lumbang bato (mixtures 4 and 5, Table V) will make a good vehicle for red lead.

This work was carried on at the suggestion and under the direction of Mr. George W. Heise.

## ILLUSTRATIONS

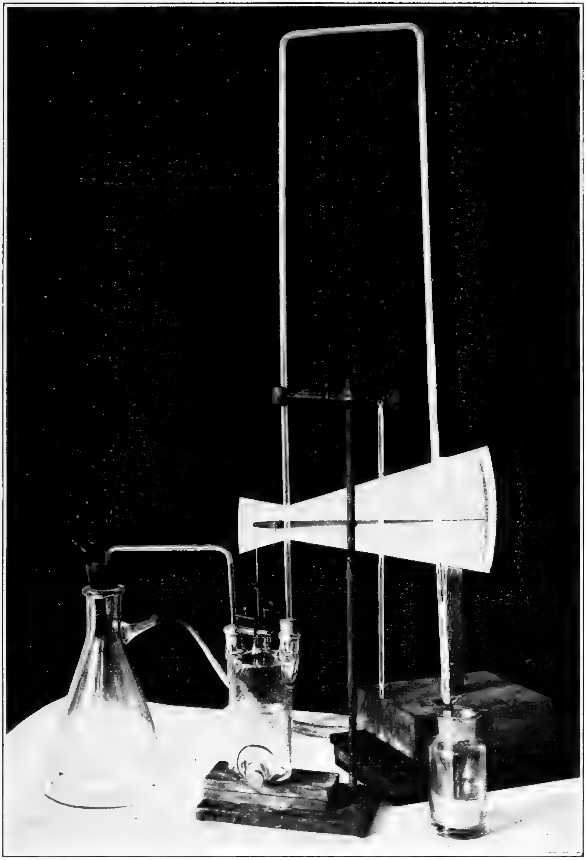

PLATE I. MODIFIED GARDNER-DE HORVATH APPARATUS.

# THE CRATER LAKE OF TAAL VOLCANO [1]

By George W. Heise

(*From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila*)

ONE PLATE AND ONE TEXT FIGURE

Previous to 1911 Taal was an active volcano, which had erupted frequently during historic times. The last and, as far as known, the greatest eruption occurred in January, 1911. An area of approximately 230 square kilometers was affected with devastating violence, (7) and over 1,300 people were killed. Since that time the volcano has been practically inactive.

The following description of the volcano was published by Adams (1) about a year before the eruption:

> Taal volcano is situated on an island in Taal or Bombon Lake. The island, on which are found a number of extinct cinder cones and the active crater, has been built near the center of the lake by late volcanic activity. * * * The main crater which is situated near the center is usually referred to as Taal volcano. It is approximately circular in form. The southwestern border of the crater rim rises to an elevation of 320 meters, which is the highest point on the island. The lowest points on the rim are about 130 to 150 meters in elevation. The lowest points on the floor of the crater are about on a level with the water of Taal Lake. * * *
>
> Two lakes lie within this crater. They are usually called the yellow lake and the green lake. During the rainy season there is a third temporary red lake. The yellow lake receives the natural drainage of the crater. It appears to be shallow and is hot, but does not boil. The green lake gives off steam from its surface and near its southern border boils violently as if over a vent. A circular crater is located to the south of the green lake. On its floor there are several boiling mud spots from which but little vapor rises. On the south border of the yellow lake there is a cone, called the red cone, because of the color of its crater. It is broken down on the south side and drains around its eastern base into the yellow lake. A vent from which steam issues with great force occurs on its northern outer base. The yellow lake now extends to this vent but formerly was separated from it by a narrow isthmus. There is a remnant of an older, large crater rim which forms a crescentic ridge rising southeast of the yellow lake and curving around to the south of the green lake, passing between the green lake and the crater with the mud spots.

Plate I, fig. 1, is from a photograph of the crater that was taken before the 1911 eruption.

[1] Received for publication June 9, 1917.

A peculiar feature of Taal Volcano is the fact that the main floor of the crater before the eruption was very nearly at sea level and that, owing to the ejection of much material during the eruption, the crater floor is now much lower. The volcano was little altered in outward appearance in the eruption of 1911, but the crater proper was greatly changed. According to the description by Pratt(7)—

The absence of vegetation and the smooth drifted surface of the ash covering which is almost white in the sunlight, give the island an appearance of a vast snow heap. The crater rim is unbroken and save for minor fissures and cracks is intact. * * *

The interior of the crater has been transformed. * * * The well-known Green Lake and Yellow Lake, which were small bodies of water, one of which (Yellow Lake) was quite shallow, referred to in descriptions of Taal since earliest historic times, are gone. In the position of the former Green Lake there is a new one, the water of which appears milky-white, due to suspended solid matter. The level of this lake was on February 17 approximately 70 meters below that of the sea. Green Lake had stood 5 meters above sea level. Two streams of hot water, the combined flow of which was estimated at 100 to 150 cubic meters per minute, were pouring into the lake. These streams came out of the crater walls about 50 meters above the lake level, seeping from just over a layer of fine-grained, impervious, bedded tuff. On the west shore of the lake a conical rock 50 to 70 meters in diameter rose to a height of 115 meters above the lake level. The upper 50 meters of this natural obelisk appeared to be bedded tuff, but the lower portion is massive basalt. A week later, the streams pouring into the crater lake had increased both in volume and in number, and the lake itself had risen apparently about 5 meters. * * *

Although hot and heavily mineralized, the water which is flowing into the new crater probably is seepage from Lake Bombon through the crater walls. Since Lake Bombon stands a few meters above sea level, the new crater lake will probably rise in time to about sea level.

A comparison of the old and new craters is shown in fig. 1.

As predicted, the water entering the crater formed a single new lake, leaving no trace of the small lakes previously present (Plate I, fig. 2). This new lake, which is over a kilometer in width and at least 70 meters deep, has no visible inlet nor outlet. The following description was written by Gates,(6) in 1914:

It [the crater] is about 2.3 kilometers long and 1.7 kilometers wide at the top. More than half of the bottom is occupied by a lake, whose elevation is about 2.5 meters above sea level, the same as that of the surrounding Lake Bombon. The water of the crater lake is clear, although dark colored, and salty. Its temperature decreased from about 37° C. in October, 1913, to about 32° in April, 1914. Swimming in it, although much like salt water bathing, was of course more exciting. Very little steam, if any, arose from the lake in either October or December, 1913, but in April, 1914, some steam was noticed arising from a few places along the shore of the lake, as well as from small vents in the north crater wall, both

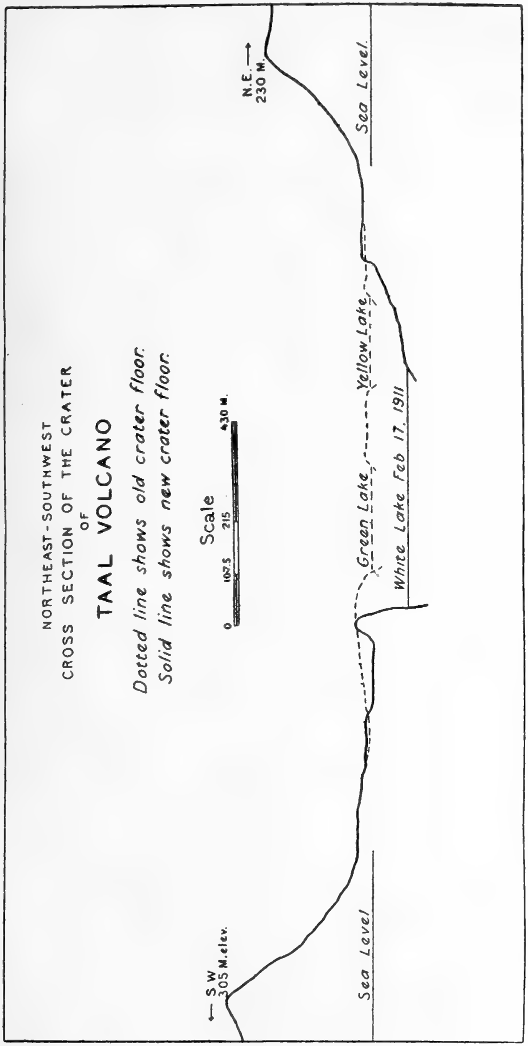


FIG. 1. Superimposed cross sections of crater before and after the 1911 eruption.

inside and outside the crater. From certain points on the crater rim sulphurous odors are noticeable, but none were detected in the bottom of the crater. Steep precipitous walls formed the boundary of the crater on all sides. At the foot of the walls, especially on the east side, large quantities of ash and mud have been washed down and have accumulated. The crater rim is highest on the south and north sides with altitudes of 304 and 230 meters, respectively. Nearly all of the west side is low, the minimum elevation being about 95 meters. There are other low points on the east side.

The above description holds very well for the conditions in the crater at the present time. There is a faint "sulphurous" smell at various points, due to mineral decomposition, and there are a number of small steam vents, principally on the north crater wall and at the west shore of the lake. Most of these vents were not readily accessible at the time the crater was visited, but on the northwest shore there were some very small openings, from which faint wisps of steam issued, and places where the sand, under water, was hot to the touch. As evidence of the insignificance of the present activity, it may be mentioned that the temperature of the lake was about 30° C., which is only a few degrees above that of ordinary surface waters in the Luzon lowlands.

There are also a few steam vents at various points on the outer slope of the volcano, and there is at least one under water, on the northern shore of the island. These, too, are insignificant. The presence of steam vents under water has given rise to the belief that there are hot springs at various points. So far as could be determined, there is no foundation for this belief.

Crystals of calcium sulphate, of iron salts, and of sulphur are found on the walls and floor of the crater, the first being abundant, the last very rare. Calcium sulphate is very plentiful, especially near the shore of the crater lake, where it has apparently been deposited from the water in large sheets a half centimeter in thickness.

Analyses of the waters of the crater previous to the 1911 eruption have been published by Centeno, in 1885,(4) and by Bacon, in 1906(2) and 1907.(3) The analysis of a sample of water from the stream flowing into the crater soon after the eruption was published by Cox.(5)

Bacon(4) made qualitative tests for radioactivity in the waters and their sediments and found that the water and sediment from the old "green lake" were very feebly active, the other waters and sediments showing no activity. Wright and Heise(8) were unable to detect the presence of radium in the water of the present crater lake.

The results of the most recent analyses of samples taken by me in February and April, 1917, are given in Table I, coupled, for comparison, with the older analyses. The analysis of the water from Lake Bombon is also shown.

A comparison of the above analyses shows that the crater waters became progressively more salty before the eruption; that immediately after the eruption, as might be expected, the water entering the crater was much less highly mineralized; and that the salt concentration has greatly increased since that time.

The crater lake is at approximately the same level as Lake Bombon, that is, a few meters above sea level, and must be over 70 meters deep. There are no indications of any springs, or of ingress of water other than that which would normally occur in an excavation extending below the water table. The crater is, in effect, a huge basin exposed to insolation.

There is, however, a large volume of water added to the lake through the rainfall, which, in this region, averages about 1,900 millimeters (75 inches) per year. The rainwater, running down the inner slope of the crater and into the lake, leaches the soluble salts from the volcanic ejecta forming the crater walls, increasing the amount of salts in the water; the intense tropical sunlight stimulates evaporation. Thus the lake water becomes more concentrated. This alternate addition of salt and evaporation of water is sufficient to account for the increasing concentration of the lake water.

The quantity of soluble salts in the soil of the volcano may be inferred from the fact that large areas on the outer slopes are still practically unvegetated, except for occasional tufts of coarse grass, and that the inside of the crater is barren, except in isolated places. On the outer slope of the volcano, the soil, 5 to 20 centimeters below the surface, still shows, six years after the eruption, large quantities of soluble matter. Analyses of the water-soluble constituents of two soil samples—one from a typical unvegetated area on the west slope of the volcano and one from a typical grass area from the west shore of the island—are given in Table II. For comparison, two analyses (5) of the water-soluble material in fine ash and ejecta, collected soon after the eruption, are shown.

TABLE I.—*Analyses of*

[Results expressed as grams per

| | Year. | | | |
|---|---|---|---|---|
| | 1885 | 1885 | 1906 | 1906 |
| Authority | Centeno[4] | Centeno[4] | Bacon[2] | Bacon[2] |
| Source | Yellow Lake[a] | Green Lake[a] | Green Lake. | Yellow Lake. |
| Color | | | Green | Yellow |
| Specific gravity at 15° C | | | 1.1062 | 1.1763 |
| Acidity | | | 1.128 N | 2.08 N |
| Acidity calculated as $H_2SO_4$ | 0.16[b] | | 6.14[b] | 10.28[b] |
| Acidity calculated as HCl | | 0.894 | 4.65[b] | 7.57[b] |
| Total solids, filtered water | | | 15.8678 | 25.7235 |
| Total solids, unfiltered water | 2.6988 | 6.0022 | 15.9312 | 30.3175 |
| Sediment (by difference) | | | 0.0634 | 4.5940 |
| Silica ($SiO_2$) | 0.0640 | 0.0740 | | |
| Iron and aluminium oxides ($Fe_2O_3$+ $Al_2O_3$). | | | | |
| Iron (Fe) (total) | | | 1.031 | 1.711 |
| Iron (ferrous) | 0.1315 | 0.3036 | 0.7150 | 1.3250 |
| Iron (ferric) | 0.0209 | 0.0612 | 0.3160 | 0.386 |
| Manganese (Mn) | | | | |
| Aluminium (Al) | 0.0143 | | 1.1892 | 3.485 |
| Calcium (Ca) | 0.0150 | 0.0136 | 0.0934 | 0.1042 |
| Magnesium (Mg) | 0.0264 | 0.0335 | 0.9432 | 1.8210 |
| Sodium (Na) | 0.6471 | 1.2405 | 1.7217 | 0.9343 |
| Potassium (K) | 0.0372 | 0.1821 | 0.0418 | 0.0514 |
| Chlorides (Cl) | 1.2873 | 3.4596 | 6.3143 | 11.2760 |
| Bromides (Br) | | | | |
| Iodides (I) | | | | |
| Sulphates ($SO_4$) | 0.4122 | 0.4186 | 4.1303 | 5.6768 |
| Phosphates ($PO_4$) | 0.0396 | 0.0515 | 0.0273 | 0.0391 |
| Loss on evaporating to total solids (?) | | | | |
| Lithium | | | | |
| Borates ($BO_2$) | | | | |
| Arsenates ($AsO_4$) | | | | |

[a] Analytical results are given as recalculated by Bacon. (2)
[b] Per cent.
[c] Analyzed by J. Gonzalez Nuñez, chemist, Bureau of Science.
[d] Normal carbonate (as $Na_2CO_3$), 24; bicarbonates (as HCO3), 150.

*waters from Taal Volcano.*

100 cubic centimeters except as noted.]

| Year. | | | | | |
|---|---|---|---|---|---|
| 1907 | 1907 | 1907 | 1911 | 1917 | 1917 |
| Bacon[(3)] | Bacon[(3)] | Bacon[(3)] | Cox[(5)] | | |
| Boiling crater lake. | Green pool, north of boiling lake. | Green Lake | Stream | Crater Lake [c] | Lake Bombon (parts per million). [d] |
| Light grayish green. | Green | Green | Milky | 90 | Nil. |
| 1.072 | 1.081 | 1.158 | | 1.023 | |
| 1.33 N | 1.335 N | 1.78 N | 0.0069 N | 0.0147 N | Nil. |
| 6.52 [b] | 6.54 [b] | 8.72 [b] | | 0.0100 N | |
| 4.84 [b] | 4.87 [b] | 6.49 [b] | | | |
| 8.576 | 10.1402 | 19.788 | | | |
| | | | | 4.000 | 1540. |
| | | | | 0.0025 [e] | 75. [e] |
| | | | 0.07108 | 0.0410 [f] | 10. |
| | | | | 0.0360 | 2. |
| 0.5157 [b] | 0.9210 [b] | 1.3446 [b] | 0.01720 | 0.0135 | 0.14. |
| 0.5148 [b] | 0.8367 [b] | 1.1960 [b] | | | |
| 0.0009 [b] | 0.0843 [b] | 0.1486 [b] | | | |
| | | | 0.00799 | 0.0310 | |
| 0.7622 [b] | 0.8978 [b] | 2.0927 [b] | 0.00261 | 0.0086 | 0.95. |
| 0.2813 [b] | 0.2082 [b] | 0.1328 [b] | 0.05568 | 0.0860 | 64. |
| 0.0318 [b] | 0.4343 [b] | 0.1514 [b] | 0.09093 | 0.2650 | 50. |
| 0.7419 [b] | 0.7192 [b] | 2.3246 [b] | 0.25843 | 0.9870 | |
| 0.0125 [b] | 0.0048 [b] | 0.0104 [b] | 0.02374 | 0.0870 | |
| 4.7512 [b] | 4.8925 [b] | 10.9312 [b] | 0.60243 | 1.830 | 580. |
| | | | Trace | Trace | |
| | | | None | 0.00005 | |
| 3.0808 [b] | 1.9688 [b] | 2.3542 [b] | 0.27320 | 0.330 | 194. |
| | | | None | 0.0018 | |
| 2.1171 [b] | 0.8284 [b] | 0.8985 [b] | | 0.6000 [g] | |
| | | | None | Nil | |
| | | | Small | do | |
| | | | do | do | |

[e] Determined turbidimetrically.
[f] Determined by evaporation with hydrofluoric acid.
[g] Loss on ignition.

TABLE II.—*Analyses of water-soluble constituents of Taal ejecta and soils.*

[Numbers give percentages by weight of air-dried sample.]

| | 1911 | | 1917 | |
|---|---|---|---|---|
| | Ash.(4) | Ejecta.(5) | Soil from unvegetated area. | Soil from grass area. |
| Silica ($SiO_2$) | 0.82 | 0.95 | 0.12 | 0.03 |
| Iron and aluminium oxides ($R_2O_3$) | 0.01 | trace | 0.03 | nil |
| Lime (CaO) | 0.16 | 0.32 | 3.81 | 0.04 |
| Magnesia (MgO) | none | none | trace | trace |
| Soda ($Na_2O$) | 1.51 | 2.03 | | |
| Potash ($K_2O$) | 1.34 | 1.25 | | |
| Manganese oxide ($Mn_3O_4$) | trace | trace | | |
| Sulphuric anhydride ($SO_3$) | 0.80 | 0.60 | 4.33 | 0.11 |
| Phosphoric anhydride ($P_2O_5$) | none | none | | |
| Chlorine (Cl) | 0.74 | 0.95 | 0.03 | 0.02 |
| Acidity (in terms of $CaCO_3$) | | | 0.16 | 0.04 |
| Total soluble material | | | 8.75 | 0.88 |

Apparently the two sets of analyses are not strictly comparable because of the length of time between them and because of the probability that somewhat different materials were tested. It is significant, however, that the amounts of chlorides, that is, of the more soluble substances, are present in much smaller quantities in the 1917 samples than in those of 1911, indicating the extent to which leaching has taken place. Sodium and potassium, though not quantitatively determined in the later analyses, could not have been present as more than traces. The difference between the two 1917 analyses is of interest and furnishes at least a partial explanation for the differences in vegetation on different portions of the island. The acidity and the high soluble salt content, over six years after the eruption, indicate that a still greater salt concentration in the crater lake may be expected.

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3. IDEM. The crater lakes of Taal Volcano, ibid., *Sec. A* (1907), 2, 115–127.
4. CENTENO, J. Estudio geológico del volcán de Taal. Madrid (1885).
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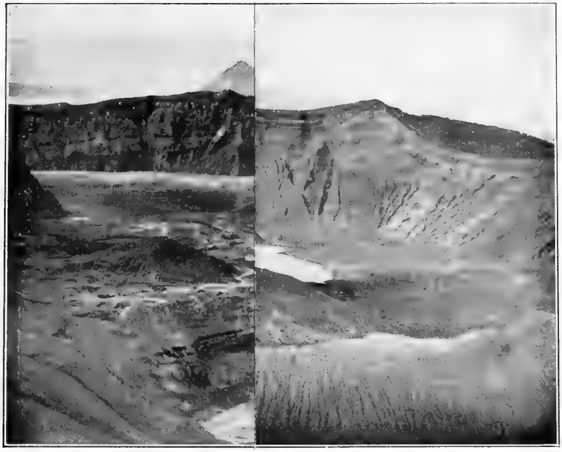
6. GATES, F. C. The pioneer vegetation of Taal Volcano, ibid., *Sec. C* (1914), 9, 391–434.
7. PRATT, W. E. The eruption of Taal Volcano, ibid., *Sec. A* (1911), 6, 63–86.
8. WRIGHT, J. R., and HEISE, G. W. The radioactivity of Philippine waters, ibid., *Sec. A* (1917), 12, 145.

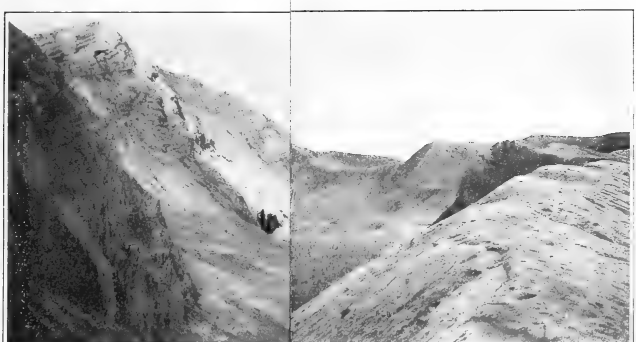
## ILLUSTRATIONS

PLATE I



TEXT FIGURE





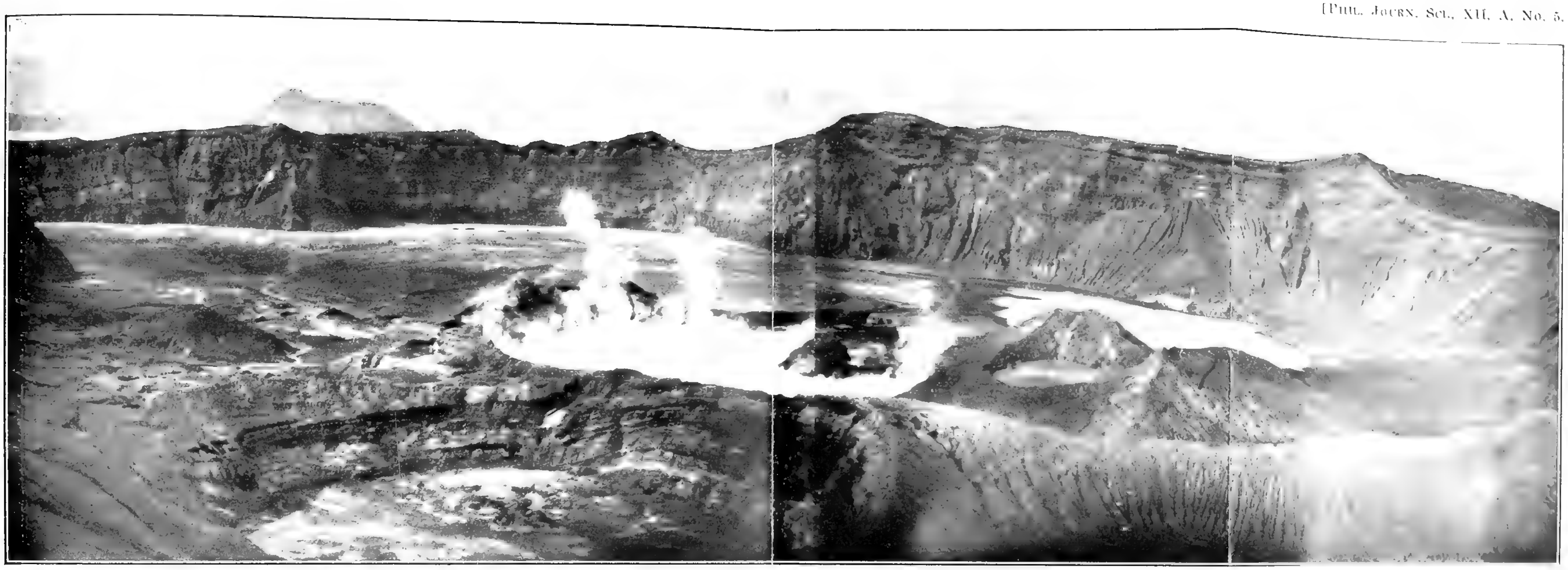


Fig. 1. Crater of Taal Volcano from the southeast, March, 1907.

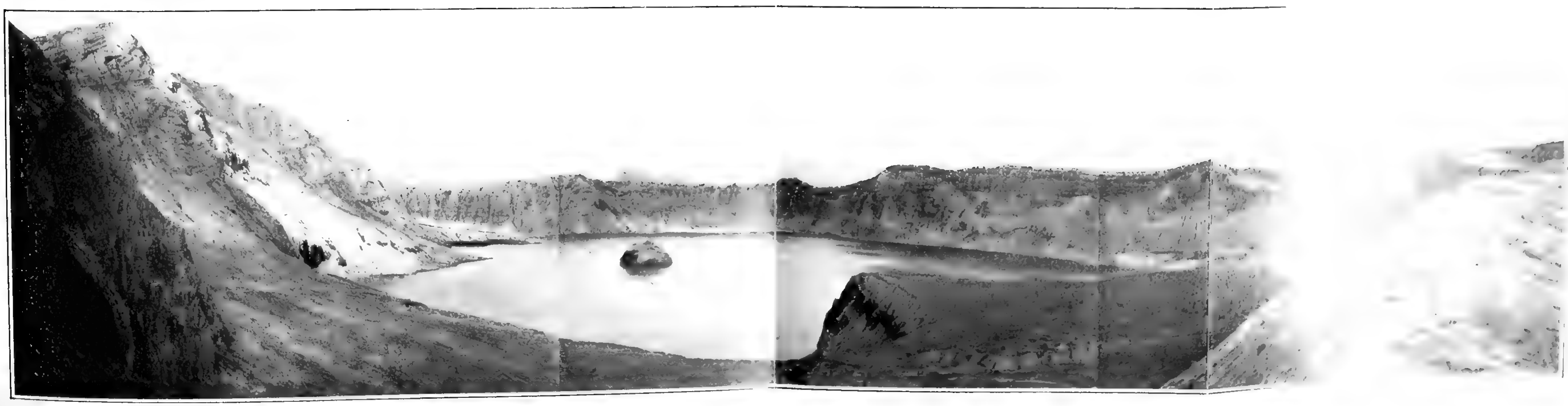


Fig. 2. Panoramic view from the south rim of the crater of Taal Volcano.

PLATE I.

# COMPOSITION OF BRICK AND MORTAR IN THE GREAT WALL OF CHINA [1]

By J. C. Witt

*(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila)*

ONE PLATE

During a recent trip to northern China I visited the Great Wall at Shanhaikwan. At this point the wall is largely composed of gray brick laid with lime mortar. The bricks have a porous structure, somewhat resembling pumice, and are much larger than ordinary building bricks. They are so weak that pieces may be easily broken off with the fingers. The mortar is pure white, under the exposed surface, and is much stronger than the brick.

The materials were of special interest to me because of recent research in ceramics and lime-burning at the Bureau of Science. A sample of each was taken and analyzed in this laboratory. The construction of the wall began in the third century before Christ, but was repaired eighteen centuries later. Therefore there was no means of knowing the age of the materials sampled, but apparently they were a part of the original structure. The general condition of the wall at this point is very good, as can be seen from Plate I, though near the top a number of the bricks are missing. Table I shows the analytical results.

TABLE I.—*Analysis of brick and mortar.*[a]

| Determination. | Brick. | Mortar. |
|---|---|---|
| | *P. ct.* | *P. ct.* |
| Loss on ignition | 0.10 | 43.88 |
| Silica ($SiO_2$) | 73.02 | 2.12 |
| Iron and aluminium oxides ($Fe_2O_3$, $Al_2O_3$) | 18.96 | 0.44 |
| Calcium oxide (CaO) | 1.29 | 48.83 |
| Magnesium oxide (MgO) | 1.05 | 4.03 |
| Sodium and potassium oxides ($Na_2O$, $K_2O$) | 5.73 | 0.85 |

[a] Analyzed by F. D. Reyes, inorganic chemist, Bureau of Science.

The brick is said to have been dried in the sun only. This was confirmed in the laboratory tests, because on ignition the material becomes dark red. If it had been originally burned in a kiln, the appearance of the wall would have been considerably different, and the strength and durability would doubtless have been much greater. Both the general appearance and the analysis of the mortar indicate that no sand was mixed with the lime. It is apparent also that the stone from which the lime was made was of good quality.

[1] Received for publication May 16, 1917.

## ILLUSTRATIONS

### PLATE I

FIG. 1. The Great Wall of China, showing location near top of wall at which samples were taken, January 4, 1917.

2. View at base of wall.

3. The wall extends over mountains and across valleys.

Fig. 1. The Great Wall of China, showing location near top of wall at which samples were taken, January 4, 1917.

Fig. 2. View at base of wall.

Fig. 3. The wall extends over mountains and across valleys.

PLATE I.

# SOME LIMITATIONS OF THE KJELDAHL METHOD[1]

By Harvey C. Brill and Francisco Aggaoili

*(From the Laboratory of Organic Chemistry, Bureau of Science, Manila)*

It is an interesting fact that the various chemistry textbooks dealing with analytical methods[2] in describing the Kjeldahl method for the determination of the nitrogen of nitrogenous organic compounds cite only hyrazine, nitro, and similar nitrogen and nitro-oxygen groups as the exceptions, which require special treatment before their total nitrogen can be obtained by this process.

Recent investigations have shown that compounds other than those enumerated in the above references are resistant to decomposition when subjected to treatment according to the Kjeldahl method or some of its modifications. Pyridine sulphonic acids are prepared by heating pyridine with sulphuric acid.[3] The yield is increased by the addition of certain metallic sulphates. This increase results from the raising of the temperature of the sulphuric acid solution due to the presence of the sulphate and possibly from the catalytic action of the latter. But more of the sulphonic acid derivative is synthesized in the presence of the sulphate at the higher temperature than in its absence.

[1] Received for publication March, 1917.

[2] In *Bull. U. S. Dept. Agr.* (1912), **107**, 5, is the following in regard to applicability of the Kjeldahl and the Gunning methods: "Not applicable in the presence of nitrates." Sudborough, J. J., and James, T. C., in Practical Organic Chemistry, Van Nostrand Company, New York (1908), 61, write: "It should be remembered the following groups of compounds do not yield quantitative results unless subjected to a preliminary treatment: Nitro, nitroso azo, hydrazo, diazonium compounds and probably cyanogen derivatives and platinichlorides of bases." Leach, A. E., Food Inspection and Analysis, John Wiley & Sons, New York (1914), 69, in discussing the use of the Kjeldahl and the Gunning methods, warns the analyst that: "Neither method in its simplest form is applicable in the presence of nitrates; if these are present, a modification must be used. The Gunning Arnold method is employed for the determination of the nitrogen in pepper, as the piperin is not completely decomposed by the usual processes."

[3] Wiedell and Wurman, *Monatsh. f. Chem.* (1895), **16**, 749. Meyer and Ritter, ibid. (1914), **35**, 765.

Funk,[4] in his study of the vitamine bodies in rice polishings, found that he obtained smaller yields of nitrogen from these compounds when the Kjeldahl method was used than when the Dumas or absolute method was used.

TABLE I.—*Nitrogen determination by means of the Kjeldahl method.*

| Compound. | Nitrogen. | | Nitrogen liberated. |
|---|---|---|---|
| | Theory. | Found. | |
| | *Per cent.* | *Per cent.* | *Per cent.* |
| Benzylcyanide | 11.96 | 11.92 | 99.73 |
| | | 11.99 | 100.00 |
| | | 11.75 | 98.25 |
| | | 11.79 | 98.59 |
| Phenylcyanate | 11.76 | 11.62 | 98.80 |
| | | 11.69 | 99.40 |
| Pyrrole | 20.90 | 17.20 | 82.30 |
| | | 16.61 | 79.47 |
| Pyridine | 17.72 | 12.18 | 68.72 |
| | | 12.19 | 68.73 |
| | | 12.34 | 69.64 |
| Piperidine | 16.47 | 11.30 | 68.63 |
| | | 9.50 | 57.69 |
| | | 12.70 | 77.12 |
| Quinoline | 10.85 | 8.41 | 77.50 |
| | | 8.79 | 81.00 |
| Isoquinoline | 10.85 | 8.58 | 79.07 |
| | | 8.48 | 76.37 |
| Oxyquinoline | 9.53 | 6.28 | 65.90 |
| | | 6.14 | 64.43 |
| Piperazine | 32.54 | 32.44 | 99.66 |
| Oxynicotinic acid | 10.00 | 10.12 | 100.00 |
| | | 9.90 | 99.00 |
| Nicotine | 17.34 | 16.93 | 97.67 |
| | | 16.85 | 97.19 |
| | | 15.89 | 91.63 |
| Methyluracyl | 22.23 | 22.25 | 100.00 |
| | | 22.55 | 100.00 |
| Allantoin | 35.44 | 34.95 | 98.60 |
| | | 34.99 | 98.73 |
| Uric acid | 33.34 | 33.39 | 100.00 |
| Caffeine | 28.35 | 28.02 | 98.82 |

Williams,[5] who was investigating this subject of compounds with antineuritic properties, at once saw the possibility of making use of this property of resisting decomposition to determine the chemical character of these compounds. As a preliminary step in the solution of this problem we undertook a determination of

[4] Funk, C., *Journ. Physiol.* (1913), 46, 177. Drummond, J. C., and Funk, C., *Biochem. Journ.* (1914), 8, 598.

[5] Williams, R. R., *This Journal, Sec. A* (1916), 11, 49.

the nitrogen content of various classes of nitrocarbon compounds by means of the Kjeldahl method to determine what type of compounds yields only a part of its nitrogen by this process.

A sample of approximately 0.2 gram of the pure compound was heated with concentrated sulphuric acid (20 to 30 cubic centimeters), potassium sulphate (5 grams), and copper sulphate (0.5 gram) for two and one-half to four hours or for one-half hour after the solution had become clear, at the boiling point of the solution. The results of this examination are given in Table I.

Benzylcyanide and phenylcyanate were included in this investigation, as it was at first thought that the low yields of nitrogen obtained might be due to the breaking down of the molecule with the liberation of hydrocyanic acid. However, it seems more plausible to attribute the low yields of nitrogen from pyrrole, pyridine, piperidine, quinoline, isoquinoline, and oxyquinoline to the formation of sulphonic acid derivatives and their subsequent resistance to decomposition by the sulphuric acid.

The use of vanadium oxide [6] has been recommended as a catalyzer in the Kjeldahl method. The method was employed by us in the determination of the nitrogen of piperidine without satisfactory results.

TABLE II.—*Nitrogen determination of piperidine by use of the modified Kjeldahl method.*[a]

| No. of analysis. | Compound. | Nitrogen. | | Total nitrogen liberated. |
|---|---|---|---|---|
| | | Theory. | Found. | |
| | | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | Piperidine | 16.47 | 12.23 | 74.26 |
| 2 | do | 16.47 | 12.15 | 73.77 |
| 3 | do | 16.47 | 12.96 | 78.69 |

[a] No 1 was prepared in the manner described by Wunder and Lascar; No. 2 had 0.5 gram of bismuth oxide substituted for the vanadium oxide; while No. 3 had the same amount of antimony oxide used as a substitute.

The results obtained in the experiment using vanadium oxide are no better than where bismuth or antimony oxide was used.

Dakin and Dudley [7] state that piperidine by prolonged heating with sulphuric acid in the presence of potassium sulphate and copper sulphate gives up all its nitrogen, but that pyridine gives less satisfactory results. In the determination of the nitrogen

[6] Wunder, W., and Lascar, O., *Journ. Pharm. et Chim.* (1914), 19, 329.

[7] Dakin, H. D., and Dudley, H. W., *Journ. Biol. Chem.* (1914), 17, 275.

content of coal, Fieldner and Taylor [8] found that low results were always obtained when the digestion was stopped as soon as the solution became colorless.

We have used piperidine with potassium sulphate and different amounts of mercuric oxide and with sodium sulphate and different amounts of mercuric oxide without quantitative yields, even when the mixture was heated for a period of ten hours.

TABLE III.—*Nitrogen determination of piperidine by a modified Kjeldahl method.*

| No. of sample. | Sodium sulphate. | Potassium sulphate. | Mercuric oxide. | Time heated. | Nitrogen. | | Total nitrogen liberated. |
|---|---|---|---|---|---|---|---|
| | | | | | Theory. | Found. | |
| | *Grams.* | *Grams.* | *Grams.* | *Hours.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 0 | 8 | 0.3 | 10 | 16.47 | 12.63 | 76.69 |
| 2 | 0 | 8 | 0.7 | 10 | 16.47 | 13.22 | 80.27 |
| 3 | 8 | 0 | 0.3 | 8 | 16.47 | 12.46 | 75.65 |

The above methods were unsuccessful in giving quantitative yields.

Finally the method known as the Gunning-Arnold method, which is recommended by Leach, [9] for the determination of the nitrogen in black pepper, was employed. This method gives good results with pyridine when the heating is continued for a considerable period after the solution becomes clear. An attempt was made to substitute sodium sulphate for the potassium sulphate in the Gunning-Arnold method, but the substitution was unsuccessful.

TABLE IV.—*Nitrogen determination of pyridine by the Gunning-Arnold method and by a modified Gunning-Arnold method.*

| No. of sample. | Sodium sulphate. | Potassium sulphate. | Time heated. | Nitrogen. | | Total nitrogen liberated. |
|---|---|---|---|---|---|---|
| | | | | Theory. | Found. | |
| | *Grams.* | *Grams.* | *Hours.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 1 | 16 | 0 | 4 | 17.72 | 12.7 | 71.6 |
| 2 | 16 | 0 | 4 | 17.72 | 12.0 | 62.1 |
| 3 | 16 | 0 | 4 | 17.72 | 13.6 | 76.2 |
| 4 | 16 | 0 | 4 | 17.72 | 15.8 | 89.2 |
| 5 | 0 | 16 | 4 | 17.72 | 17.2 | 96.5 |
| 6 | 0 | 16 | 4 | 17.72 | 17.6 | 99.3 |
| 7 | 0 | 16 | 3½ | 17.72 | 16.6 | 93.6 |
| 8 | 0 | 16 | 3½ | 17.72 | 16.3 | 92.0 |

[8] Fieldner, A. C., and Taylor, C. A., *Journ. Ind. & Eng. Chem.* (1915), 7, 106.

[9] Loc. cit.

The results when sodium sulphate was used are in every case low. Digesting the pyridine for a longer time is conducive to more nearly theoretical yields. Where mercury is used, care must be taken to precipitate it as the sulphide. A loss in nitrogen is liable to arise from this source, because of the difficulty of decomposing the ammonio-mercurial compound.[10]

SUMMARY

The Kjeldahl method gives low results for nitrogen with pyridine, piperidine, quinoline, isoquinoline, oxyquinoline, pyrrole, and in some cases with nicotine. The authors believe this arises from the formation of sulphonic acid derivatives and their resistance to decomposition.

The Gunning-Arnold method gives more reliable results with pyridine when heated for a considerable period after the solution has become clear.

Sodium sulphate is not conducive to good yields and cannot be substituted for potassium sulphate.

[10] Justin-Mueller, Ed., *Bull. Sci. Pharm., Paris* (1916), 23, 167. Nolte, Otto, *Zeitschr. f. anal. Chem.* (1916), 55, 185.

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## ALCOHOL FROM DISCARD MOLASSES IN THE PHILIPPINE ISLANDS[1]

By HARVEY C. BRILL AND LEAVITT W. THURLOW

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila*)

The utilization of the discard molasses of the sugar mill is yearly becoming of more importance. Several uses suggest themselves.

1. Molasses has value as a cattle food. Its application to this use depends on local conditions of freight rates and whether it is to be transported long distances or consumed near where it is produced. At present very little is thus utilized in the Philippine Islands, although this use may have possibilities, for in the United States molasses for this purpose, inferior to the Philippine products, sells at a greater price even though it is shipped considerable distances.

2. Attempts have been and are being made to use it for fuel. In Honolulu it has been burned to recover the ash for fertilizer purposes. All the phosphates and potash, except a small volatilized portion, remain. Practically all the nitrogen is lost when molasses is burned. It is difficult to handle as a fuel, because of easily fusible constituents of the ash that form a glaze on the walls of the furnace. However, since fuel is scarce in many centrals, the use of extra grate bars, effort, and expense are justifiable in the utilization of molasses as fuel.

3. Its use as a binder in paving brick is still in the experimental stage, and its usefulness for this purpose cannot be predicted at this time.

4. It has been used as a binder in the manufacture of briquettes from coal dust. Only a portion of it could be utilized

[1] Received for publication May, 1917.

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in the manufacture of briquettes were the enterprise ever so successful, and as coal dust [2] promises to be extensively used per se for fuel purposes, no great quantities of molasses are likely to be used for the manufacture of briquettes from coal dust.

5. Molasses is valuable per se as a fertilizer, but in this use too much sugar is wasted and the effects of the sugar on the soil are not altogether beneficial. The bacteria [3] that fix nitrogen in the soil independently of the host plant are stimulated by sugar, especially glucose. One should expect to be able so to stimulate the bacteria by the use of molasses that the nitrogen fixation from this source would become important. All attempts to do this have been disappointing, since the sugar likewise stimulates the class of bacteria that breaks down the stored-up nitrogen compounds.

6. If the molasses were first fermented, it would yield a profit from the alcohol obtained and the lees would become a valuable source of fertilizer, because of their nitrogen, potash, and phosphate content. The making of alcohol from molasses and the recovery of the fertilizing ingredients is the most profitable of the known uses for molasses.

All the fertilizing ingredients ordinarily removed from the soil by the cane are concentrated in the molasses, so that when these are recovered and returned to the soil, together with the ash from the fiber or bagasse, the soil has suffered no loss and theoretically is as capable of producing a second crop as it was of producing the preceding one. The sugar industry is unique in that the sugar produced represents no constituent taken from the soil that must be returned in the form of fertilizer. Consequently, if the mineral ingredients found in the bagasse and in the molasses are returned to the soil, the soil is no more depleted than before the crop was harvested. Discard molasses in the Philippine Islands sells for about 6 centavos [4] a gallon (1.6 centavos a liter), or about 10 pesos a ton. Peck and Noel Deerr [5] have estimated the value of the fertilizer ingredients in 1 ton of Hawaiian molasses at 14 pesos and the cost of the recovery of these constituents at 6 pesos.

[2] The Chicago & North Western Railway Co. is successfully using coal dust in running one of its engines. It claims to obtain higher efficiency from coal dust than from lump coal.

[3] These are a different group from those existing in the nodules of legumes.

[4] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

[5] *Bull. Hawaiian Exp. Station,* 26, through *Sugar* (1914), 16, No. 7, 38.

TABLE I.—*Fertilizer constituents of Philippine and of Hawaiian molasses.*

| Constituent. | Philippine. | Hawaiian. |
|---|---|---|
| | *Per cent.* | *Per cent.* |
| Potash | 1.39 | 3.99 |
| Phosphorus | 0.38 | 0.21 |
| Nitrogen | 0.21 | 0.64 |

The potash and nitrogen content are greater for Hawaiian molasses than for Philippine molasses. The Hawaiian cane takes up more of these constituents, because the quantity available is greater due to the general use of fertilizers in the Hawaiian Islands. In many cases no fertilizer is added to the sugar lands of the Philippine Islands and no attempt is made to return the fertilizer ingredients found in the ash of the bagasse and in the molasses. Thus it is only a question of years before fertilization must be practiced, or this land will become exhausted and the planters' loss will be much larger than at present on account of the smaller crops resulting. Therefore it is expected that the fertilizer value will never be lower than now.

In practice about 1 ton of molasses is produced for every 5 to 6 tons of centrifugal sugar. During 1915, 211,012,817 kilograms of sugar were exported from the Philippine Islands. Were this exportation all centrifugal sugar, it would represent over 30,000,000 kilograms of molasses. If this molasses were converted into alcohol and the fertilizer ingredients were recovered from the lees, they would be worth more than 125,000 pesos at the price quoted for the fertilizer ingredients in Hawaiian molasses,[6] while the alcohol would represent a value of, approximately, 1,750,000 pesos calculated at 17.2 centavos, the current (December 1, 1916) selling price per liter of 182 proof denatured alcohol.

A considerable portion of the Philippine discard molasses is now being used for the manufacture of alcohol, and several concerns are planning to extend their activities so that the waste here is not greater than in many other sugar-growing countries. The methods of fermentation are crude and capable of much improvement. For example, no well-directed effort is made to keep an accurate control of the percentage yields by determining the sugar content of the molasses and by diluting the wort to a definite strength. Care is seldom taken to keep the vats and machinery clean or to sterilize the vats, and even com-

[6] Peck and Deerr, loc. cit.

mon cleanliness is often strikingly lacking. Neither the inoculation of the wort with a culture of yeast in order that the yeast may have a start on the bacteria, nor the distillation of the ferment when the alcohol content is at a maximum, is always carried out. It is common practice to allow the wort to become inoculated with yeast from the air. From one to three days are required to bring about active fermentation, and as a consequence the ferment becomes infested with bacteria, which destroy much of the sugar before the yeast crowds them out. No attempt is made to use good water for diluting the molasses, and it is a common practice to use dirty water, thus introducing large quantities of bacteria. Poor yields are obtained when poor methods are used. When the vats and solutions are sterilized, when pure cultures are used, and more care is taken, the cost of handling the solutions will increase, but the greater yield will more than compensate for this. Some figures presented by Owen [7] on the relation of profit to efficiency of fermentation are significant enough to be quoted here.

TABLE II.—*Profits from the fermentation of molasses, under varying conditions of efficiency.*

| Theoretical yield. Per cent. | Profit per gallon. Cents.[a] |
|---|---|
| 57 | −5.5 |
| 60 | 0.1 |
| 66 | 1.43 |
| 69 | 2.0 |
| 75 | 3.3 |
| 80 | 4.3 |
| 85 | 5.4 |
| 90 | 6.5 |
| 94.7 | 7.4 |

[a] United States currency.

This estimate is based on a cost price for Cuban molasses (total sugar as glucose, 55.11 per cent) of 10 centavos a gallon and a selling price of alcohol of 76 centavos a gallon, 180 proof. Theoretically 51.1 per cent of the weight of the sugar is the weight of the resulting alcohol, but in practice this cannot be attained, since some of the sugar is consumed by the yeast and some of it is converted into glycerol, succinic acid, cellulose, etc., so that the highest percentage possible is 94.7 per cent of the theoretical.

Table II shows that no profit results when a yield below 60 per cent is obtained from molasses under these conditions of cost and selling price. A profit of 2 centavos is not obtained until we reach an efficiency of 65 per cent. At 80 per cent, which is

[7] *Sugar* (1914), **16**, No. 7, 32.

considered good distillery practice, the profits increase to 8.6 centavos; while at 94.7 per cent of the theoretical, which is the highest possible yield obtainable, the profits have risen to 14.8 centavos a gallon, almost three times as great as the profits for a 75 per cent yield. This seemingly high increase in the profits is due to the increased yields more than compensating for the increased cost of production. In the Philippines, where the molasses [8] costs 6 centavos a gallon and 182 proof alcohol sells at 17.2 centavos a liter, the profits resulting are as given in Table III.

TABLE III.—*Profits from the fermentation of Philippine molasses under varying conditions of efficiency.*

| Theoretical yield. | Profit per gallon of molasses. Calculated on the basis of Table II. | Profit per gallon of molasses. Based on the estimated cost of alcohol production in the P. I.[a] |
|---|---|---|
| *Per cent.* | *Centavos.* | *Centavos.* |
| 57 | 5.8 | 4.5 |
| 60 | 7.0 | 5.7 |
| 65 | 8.9 | 7.6 |
| 70 | 10.8 | 9.5 |
| 75 | 12.7 | 11.4 |
| 80 | 14.6 | 13.3 |
| 85 | 16.6 | 15.3 |
| 90 | 18.5 | 17.2 |
| 94.7 | 20.3 | 19.0 |

[a] Calculated on the basis of a cost of 17.3 centavos for converting 1 gallon of molasses into alcohol.

The cost of converting 1 gallon of molasses in the United States into 90 per cent alcohol is 16 centavos. The estimate as deduced from certain data collected in the Philippine Islands makes the cost 17.3 centavos, only slightly greater than the above, and leaves a good margin of profit for the manufacturer. The larger profit for alcohol produced in the Philippine Islands is due to the smaller price paid for the molasses and its higher sugar content. A yield of 80 per cent of the theoretical gives a profit on the molasses of 13.3 centavos per gallon, while a 60 per cent yield allows a profit less than half as great. Any improvement in the methods of fermentation and distillation of molasses would mean an increase of revenue to the Islands and larger profits to the manufacturers. No alarm need be felt in

[8] Average total sugar as glucose for 10 samples, 62.6 per cent.

regard to a possible overproduction of alcohol [9] in the future. It is certain to have an increased sale for power purposes with the rise in the price of gasoline. Special carburetors are sure to be invented which will be adapted for alcohol or gasoline interchangeably as a fuel. The data in Table IV are suggestive of what will take place on a large scale at no distant date.

TABLE IV.—*Data obtained in Germany with various fuels and mixtures on a model 1914 Mercedes car, ordinary carburetor.*[a]

| Fuel. | Speed, per hour. | Distance covered on 1 pint of fuel. |
|---|---|---|
| *Parts.* | *Miles.* | *Miles.* |
| 1 benzol to 1 alcohol | 42 | 4.66 |
| 1 benzol to 2 alcohol | 41 | 4.47 |
| 1 benzol to 3 alcohol | 39 | 4.34 |
| 1 benzol to 4 alcohol | 38 | 4.10 |
| 1 benzol to 5 alcohol | 36 | 3.72 |
| Benzol, pure | 42 | 3.79 |
| Gasoline, pure | 44 | 3.60 |

[a] *Chem. Eng. & Manufact.* (1916), 24, 86.

At the present price [10] of these fuels, mixtures of alcohol with benzol are economical sources of power.

England [11] produces 100 proof alcohol at a cost of 19.5 centavos per liter; Germany produces absolute alcohol at a cost of from 12.5 to 15 centavos per liter; the United States at 16 centavos a liter of 182 proof; and the Philippine Islands at 17.3 centavos a liter of 182 proof.[12] To compete with alcohol produced by Germany or the United States, the Philippine Islands must establish efficient methods in order to reduce the cost of production.

Improvements in the process of fermenting molasses must proceed along the lines of the concentration of the ferment, control of the temperature during fermentation, the kind of yeast used, including freedom from bacteria and wild yeast, and the choice and use of yeast foods and stimulants.

As fermentation is the result of the activity of living organisms, a study of the most favorable conditions for their growth and activity should result in the discovery of the environment

[9] See Cox, Alvin J., *This Journal, Sec. A* (1909), 4, 232.

[10] Cost of 90 per cent benzol per liter, 31.7 centavos; gasoline, 33 centavos; alcohol, 182 proof, 17.2 centavos. (December 1, 1916.)

[11] Martin, Industrial Chemistry, Organic. D. Appleton and Company, New York (1913), 280.

[12] Calculated from data furnished by local distillers.

most suitable for them and should result in an accompanying benefit to the distiller in the increased yields of alcohol.

In our search for a suitable yeast we were assisted by Mr. K. B. Graae, bacteriologist, Bureau of Science, who isolated five cultures of yeast from fermenting nipa juice. These afterward proved to belong to the same race of top-fermenting yeast, a *Saccharomyces*. The cells are smaller than those of race II or race XII[13] and are fairly quick-fermenting. The use of a quick-fermenting yeast is an advantage, since owing to its rapid growth it crowds out bacteria and wild yeasts.

For the growth of yeast, properly adjusted foodstuffs are necessary. A solution of pure cane sugar would undergo fermentation, but the yeast would not grow and the fermentation would stop after the enzymes already formulated by the yeast became exhausted. Yeasts require for their growth certain organic and inorganic compounds, such as nitrogen bodies (ammonium salts, amides, peptones, phosphates, sulphates, potassium, and magnesium salts), which are always present in available form in sufficient quantities in grape juice and beer wort, but not in molasses. The presence of proper food stimulates yeast growth, and rapid growth of cultured yeast prevents the development of bacteria and wild yeast. The latter are undesirable, since some of them convert the sugar into substances other than alcohol and thus lessen the yield, while others produce alcohol, but in reduced amounts. Yeast can be accustomed to the presence of the antiseptics, so that they withstand them when present in not too large quantities.[14] Advantage is taken of this fact to keep the ferment free from bacteria and wild yeast, which are much more susceptible to the influence of such reagents. Sulphuric acid and salts of hydrofluoric acid are extensively used for this purpose.

A 5 per cent solution of alcohol is strong enough to stop the propagation of many yeasts, but the enzymes continue to act for some time after the propagation of the yeast has stopped. Others by cultivation have become accustomed to more concentrated solutions; consequently they will ferment in much stronger solutions. A concentrated solution of molasses ferments more slowly after a certain period, because of this higher percentage

[13] Race II and race XII are two famous yeasts developed in Germany and used largely in continental Europe because of their ability to ferment concentrated solutions quickly.

[14] Among the antiseptics are mercuric chloride, copper sulphate, sulphurous acid, hydrofluoric acid, nitric acid, nitrous acid, salicylic acid, formaldehyde, carbon disulphide, chloroform, ether, alcohol, etc.

of alcohol, so that the fermentation period is prolonged. Extremely prolonged periods of fermentation are to be avoided, since solutions are liable to bacterial infection and consequent loss of alcohol. On the other hand, dilute solutions cost more for distillation and require more space for handling; consequently yeasts that will quickly ferment concentrated solutions are to be preferred.

The temperature for fermentation is dependent to some extent on the yeast used. Investigation has proved that temperatures below 30° C. are usually best. High temperatures are favorable for bacterial growth, especially acid-forming bacteria, and the loss of alcohol resulting from evaporation is greater. When the yeast causes fermentation, considerable heat is liberated, and unless cooling coils are used, the temperature of the fermenting vat rises. In the Philippine Islands, where the usual atmospheric temperature is 30° C., the temperature during fermentation rises as high as 45° C. in some cases.

### EXPERIMENTAL PART

The solutions of molasses used were in every case sterilized after the sulphuric acid was added. Tests were made on the yeast to determine what temperature it is capable of enduring without having its powers of reproduction destroyed. Ten per cent molasses solutions were sterilized and then inoculated from the stock culture of the yeast, with the results recorded in Table V.

TABLE V.—*Effects of heating at various temperatures for ten minutes on the yeast found in the fermenting nipa juice.*

| Flask No. | Initial treatment. | Condition at end of— | |
|---|---|---|---|
| | | 28 hours. | 48 hours. |
| 1 | Control; sterilized wort; no inoculation. | Sterile | Sterile. |
| 2 | Control; inoculated; not heated. | Solid mass of cells | Same as at end of 28 hours. |
| 3 | Inoculated; heated to 40° C. | Not so numerous as in 2 | Well developed; good condition. |
| 4 | Inoculated; heated to 45° C. | Fewer than in 3. Healthy condition. | Do. |
| 5 (in duplicate) | Inoculated; heated to 50° C. | do | Do. |
| 6 (in duplicate) | Inoculated; heated to 55° C. | Scattering clusters of cells. | Do. |
| 7 (in duplicate) | Inoculated; heated to 60° C. | do | Do. |
| 8 (in duplicate) | Inoculated; heated to 65° C. | Scattering cells<br>Condition poor | Yeast very plentiful.<br>Good condition. |
| 9 (in duplicate) | Inoculated; heated to 70° C. | No cells discernible | Sterile. |

Heating for ten minutes has a slight effect at 40° C., but the shock from heating for this length of time is not severe until

a temperature of 65° C. is reached. Yeast heated for ten minutes showed the effects of being subjected to this high temperature even at the end of the second day. The cells had not become so numerous as they were in the other cultures. A temperature of 70° C. prolonged for ten minutes destroyed their powers, so that they failed to propagate. Heating for longer intervals of time at temperatures between 45° and 65° C. will seriously impair their powers if it does not destroy them entirely, so that the temperature of the fermenting liquid should be down to 40° C. before the inoculating solution is added and should be rapidly cooled to 30° C.

Parallel tests of the five cultures of yeast isolated from fermenting nipa juice were made to determine if any difference existed in the efficiency of these cultures. Two hundred grams of molasses, of the quality shown by the data that follow, were dissolved in water, 1 cubic centimeter of concentrated sulphuric acid was added, and the whole was given a single heating. Sulphuric and hydrochloric acids have an inhibiting effect on the growth of wild yeasts and bacteria; consequently small quantities of these are usually added. After sterilization the contents were made up to 1 liter, 0.27 gram of ammonium sulphate was added, and the solution was inoculated with 10 cubic centimeters of the inoculating solution. This will be called the standard solution for Table VI. The samples were run in duplicate at a temperature of 30° C. They differed from each other in that the second one of each yeast contained 0.06 gram of sodium fluoride to the liter. The comparisons were made by removing 100 cubic centimeters of the ferment, adding 100 cubic centimeters of water, and distilling exactly 100 cubic centimeters of the mixture and determining the alcohol content by the use of the Westphalt balance at 15.6° C. at the end of definite periods of time. The acidity determinations were made by titrating 10 cubic centimeters of the ferment with 0.1 *N* alkali solution, using phenolphthalein as an indicator. It is, therefore, expressed in cubic centimeters of 0.1 *N* alkali necessary to neutralize 10 cubic centimeters of the ferment. The alcoholic content is given in percentage by volume. The cell count is comparative and is the number of millions per cubic centimeter of ferment. In Table VI the analysis of the molasses used throughout the laboratory experiments is given.

The acidity of the ferment could not be determined with extreme accuracy because of the dark color of the ferment and the difficulty of observing color changes. The highest acidity corresponds to the lowest alcohol content, showing that the

TABLE VI.—*Data on the molasses used in the laboratory experiments.*

| | °C. | Per cent. |
|---|---|---|
| Direct polarization | 31.9 | |
| True sucrose | | 38.1 |
| Reducing sugars | | 21.6 |
| Total sugar calculated as glucose | | 61.6 |
| Total nitrogen | | 0.2 |
| Total phosphoric acid | | 0.38 |
| Potash | | 1.39 |
| Calcium | | 0.53 |
| Magnesium | | 0.11 |

acidity increases at the expense of the alcohol. The cell count at the end of sixteen hours is low in the samples that give a low yield of alcohol. The alcohol content is dependent on the number of cells. The alcohol content for the five cultures is fairly constant. The difference can well be accounted for by slight differences in the vigor of the yeast caused by its previous experience in the stock-yeast solution. All had the same appearance under the microscope and reacted identically in the wort, which justifies the conclusion that they are the same. The maximum yield of alcohol is not reached until the end of the fourth day. The results recorded in Table VIII are for the standard solutions made up of the same concentrations of molasses and sulphuric acid as for Table VII (2 grams per liter solution) with the addition of varying amounts of ammonium fluoride. Three of these were kept at an average temperature of 36° C., while the others were at room temperature (30° C.) throughout the experiment.

Ammonium salts increase the activity of yeast, while fluorides [15] are reputed to stimulate the yeast and prevent the growth of bacteria and wild yeast.

The data in Table VIII indicate that high temperatures result in a loss of alcohol and also that greater action of bacteria takes place. The beneficial action of ammonium fluoride is well brought out in the higher yields from samples 5, 6, and 8, where the larger amounts of this salt were added in comparison with 7, which had no salt, fermented slowly, and had a comparatively low yield. The influence of the fluoride was evident in the freedom from bacteria of samples 5, 6, and 8, and in the presence of many bacteria in 7 and somewhat less contamination in 4, where only a small amount of the salt was added. The slow fermentation is due to the small amount of nitrogen food present. In Table VII, where larger amounts of ammonium salts

[15] Backeland, L. H., *Journ. Am. Chem. Soc.* (1892), 14, 212.

TABLE VII.—*Comparative results of the five cultures of yeast cells isolated from fermenting nipa juice.*

| Yeast No. | Sodium fluoride added to 1 liter of standard solution. | 16 hours. | | 40 hours. | 64 hours. | | 88 hours. | | | 112 hours. | | 136 hours. | | Alcohol. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al-cohol. | Cells. | Al-cohol. | Al-cohol. | Acid-ity. | Al-cohol. | Cells. | Acid-ity. | Al-cohol. | Acid-ity. | Al-cohol. | Acid-ity. | Maxi-mum content, | Yield, per cent of theo-retical. |
| | g. | | | | | | | | | | | | | | |
| 1 | none | 1.06 | 70.0 | 3.91 | 4.49 | 8.92 | 5.46 | 33.4 | 8.82 | 6.69 | 8.80 | 6.23 | 8.84 | 6.69 | 89.9 |
| 1 | 0.06 | 0.84 | 68.8 | 3.97 | 5.99 | 8.36 | 6.15 | 29.3 | 8.52 | 6.46 | 8.76 | 6.23 | 8.66 | 6.46 | 87.0 |
| 2 | none | 1.12 | 72.5 | 3.76 | 5.46 | 7.48 | 6.12 | 37.9 | 8.52 | 6.46 | 8.28 | 6.23 | 8.40 | 6.46 | 87.0 |
| 2 | 0.06 | 0.84 | 63.6 | 3.34 | 5.39 | 7.80 | 6.21 | 34.2 | 8.64 | 6.15 | 8.96 | 5.61 | 8.60 | 6.21 | 83.5 |
| 3 | none | 1.12 | 77.0 | 3.91 | 5.89 | 8.76 | 6.21 | 42.8 | 8.60 | 6.38 | 8.88 | 6.39 | 8.60 | 6.39 | 86.0 |
| 3 | 0.06 | 0.84 | 84.3 | 3.91 | 4.64 | 8.60 | 5.91 | 42.0 | 9.00 | 6.62 | 9.60 | 6.07 | 9.96 | 6.62 | 89.1 |
| 4 | none | 1.12 | 72.5 | 3.62 | 4.94 | 7.80 | 6.21 | 39.3 | 9.00 | 6.31 | 9.68 | 6.31 | 9.52 | 6.31 | 85.1 |
| 4 | 0.06 | 1.06 | 85.5 | 3.62 | 5.14 | 8.92 | 6.15 | 37.3 | 8.96 | 6.78 | 9.32 | 6.46 | 9.16 | 6.78 | 91.5 |
| 5 | none | 1.19 | 69.3 | 3.34 | 4.49 | 8.72 | 5.99 | 38.5 | 8.64 | 6.38 | 9.26 | 6.54 | 9.62 | 6.54 | 87.8 |
| 5 | 0.06 | 0.99 | 64.4 | 2.99 | 3.98 | 8.12 | 4.94 | 43.2 | 9.04 | 6.15 | 10.40 | 5.69 | 10.20 | 6.15 | 82.7 |

TABLE VIII.—*Influence of varying amounts of ammonium fluoride on the fermentation of molasses.*

| Sample No. | Ammonium fluoride added. | Average temperature. | 16 hours. | | 40 hours. | 64 hours. | 88 hours. | 112 hours. | | 136 hours. | 160 hours. | Alcohol. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Alcohol. | Cells. | Alcohol. | Alcohol. | Alcohol. | Alcohol. | Acidity. | Alcohol. | Alcohol. | Maximum yield. | Yield, per cent of theoretical. |
| | g. | °C. | | | | | | | | | | | |
| 1 | none | 36 | 0.45 | 43.2 | 1.40 | 2.25 | 2.51 | 2.29 | 10.0 | | | 2.51 | 34.0 |
| 2 | 0.04 | 36 | 0.79 | 45.8 | 2.35 | 3.05 | 3.55 | 3.28 | 9.8 | | | 3.55 | 48.0 |
| 3 | 0.10 | 36 | 0.91 | 32.2 | 2.50 | 3.83 | 4.12 | 3.49 | 9.8 | | | 4.12 | 55.5 |
| 4 | 0.02 | 30 | 1.37 | 39.0 | 2.01 | 3.38 | 3.91 | 4.86 | 9.0 | 5.31 | 5.91 | 5.91 | 79.4 |
| 5 | 0.07 | 30 | 1.53 | 67.0 | 2.51 | 3.83 | 4.56 | 5.46 | 9.0 | 6.32 | 6.31 | 6.32 | 85.0 |
| 6 | 0.10 | 30 | 1.40 | 65.8 | 3.12 | 5.07 | 5.76 | 5.77 | 8.4 | 6.29 | 6.09 | 6.29 | 84.6 |
| 7 | none | 30 | 1.37 | 33.0 | 1.74 | 2.70 | 3.41 | 3.98 | 10.1 | 5.01 | 5.24 | 5.24 | 70.5 |
| 8 | 0.07 | 30 | 1.37 | 61.0 | 2.28 | 3.84 | 4.56 | 5.31 | 9.0 | 6.23 | 6.03 | 6.22 | 83.7 |

were added, the maximum alcohol content was attained at the end of the fourth day. In Table VI the maximum alcohol content was not reached at the end of the fourth day in a single instance. No effort was made to accustom the yeast to the presence of the fluoride by culture, antecedent to the experiment tabulated in Table VIII, and this partly accounts for the slowness of the fermentation.

A study of the effect of adding various inorganic salts to the ferment was made. The results of this experiment are recorded in Table IX. The standard solution used here was 200 grams of molasses made up to 1 liter, with the addition of 2 grams of sulphuric acid, and then heated to 70° C. After cooling, the samples were inoculated with pure yeast culture and the various salts were added.

Table IX shows that magnesium sulphate, sodium chloride, sodium fluoride, potassium phosphate, and sea water do not stimulate the yeast as do ammonium sulphate and fluoride. Samples 2, 3, and 4 gave the largest yields. Samples 3 and 4 had two equivalents of ammonium salts added to them, while 2 had but one. Samples 1, 5, and 9 had one equivalent of ammonium salts added; they excel the remainder of the samples that had no ammonium salts added. This is good evidence of the benefit of adding ammonium salts. Phosphates [16] stimulate yeast, so that its initial activity is increased. They apparently initiate the fermentation, that is, if the materials used in fermentation could be made absolutely free from phosphates, no fermentation would occur. The apparent noneffect caused by the addition of the phosphate in samples 8 and 9 is due probably to the presence of sufficient quantities of phosphates in the original molasses solution to accelerate the fermentation, and the addition of further quantities has no apparent effect.

The ammonium salts keep the ferment comparatively free from bacteria, because the growth of the yeast is stimulated and the bacteria are crowded out. Ammonium sulphate is as efficient for this purpose as is ammonium fluoride and is much cheaper. Sea water has a deleterious effect on the ferment.[17] The amount of alcohol produced in every case is less than where distilled water alone was used. Sample 7, Table VIII (distilled water used), gave a yield of 70.5 per cent of the theoretical, while

[16] Harden, Arthur, Alcoholic Fermentation. Longmans, Green, and Co., 39 Paternoster Row, London (1911), 50.

[17] The influence of sea water was studied, since salt water from the esteros, on which many of the distilleries are located, is often used for diluting the molasses.

TABLE IX.—*Influence of various salts on the fermentation of molasses.*

| Sample No. | Substance added to standard solution. | 16 hours. | | 40 hours. | | 64 hours. | | 88 hours. | 112 hours. | 136 hours. | | Condition in regard to presence of bacteria at end of 88 hours. | Alcohol. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Alcohol. | Cells. | Alcohol. | Cells. | Alcohol. | Cells. | Alcohol. | Alcohol. | Alcohol. | Acidity. | | Maximum yield. | Yield, per cent of theoretical. |
| 1 | 0.10 gram ammonium fluoride, 1 equivalent. | 0.91 | 90 | 2.01 | 98 | 3.41 | 99 | 4.85 | 5.65 | 9.95 | 9.02 | Clean | 5.99 | 80.5 |
| 2 | do | 0.26 | 45 | 2.56 | 77 | 3.91 | 70 | 5.18 | 6.64 | 6.37 | 7.00 | do | 6.64 | 89.1 |
| 3 | 0.20 gram ammonium fluoride, 2 equivalents. | 0.99 | 78 | 3.71 | 110 | 5.16 | 72 | 6.61 | 6.61 | 6.46 | 8.56 | Fine | 6.61 | 88.9 |
| 4 | 0.36 gram ammonium sulphate, 2 equivalents. | 1.19 | 67 | 4.56 | 150 | 6.00 | 70 | 6.61 | 6.61 | 6.54 | 9.24 | Clean | 6.61 | 88.9 |
| 5 | 0.18 gram ammonium sulphate, 1 equivalent. | 0.32 | 55 | 2.49 | 59 | 3.98 | 50 | 4.85 | 5.99 | 6.00 | 7.84 | do | 6.00 | 80.6 |
| 6 | 0.12 gram sodium fluoride, 1 equivalent | 0.58 | 36 | 2.01 | 69 | 3.27 | 33 | 4.05 | 5.24 | 5.08 | 8.20 | do | 5.24 | 70.4 |
| 7 | 0.48 gram sodium chloride, 3 equivalents | 0.91 | 33 | 2.21 | 63 | 3.27 | 38 | 3.84 | 4.79 | 5.31 | 8.64 | Fair | 5.31 | 71.6 |
| 8 | 0.34 gram potassium phosphate, 1 equivalent. | 0.36 | 31 | 2.01 | 48 | 2.98 | 38 | 3.76 | 4.34 | 5.46 | 9.64 | Clean | 5.46 | 73.4 |
| 9 | 0.34 gram potassium phosphate plus 0.10 ammonium fluoride, 1 equivalent of each. | 0.19 | 45 | 1.54 | 82 | 4.20 | 60 | 4.85 | 5.76 | 6.00 | 10.00 | do | 6.00 | 80.5 |
| 10 | 0.33 gram magnesium sulphate, 2 equivalents. | 0.52 | 39 | 2.01 | 58 | 3.05 | 39 | 3.84 | 4.79 | 5.31 | 8.72 | Fair | 5.31 | 71.6 |
| 11 | ¼ strength sea water | 0.19 | 26 | 1.00 | 68 | 2.57 | 29 | 3.19 | 3.97 | 4.71 | 7.98 | Dirty | 4.71 | 63.4 |
| 12 | ½ strength sea water | 0.52 | 36 | 1.67 | 50 | 2.63 | 39 | 3.12 | 3.84 | 4.65 | 8.00 | do | 4.65 | 62.5 |
| 13 | Full strength sea water | 0.00 | 8 | 1.12 | 56 | 2.04 | 53 | 2.42 | 3.26 | 4.12 | 8.04 | do | 4.12 | 55.5 |

samples 11, 12, and 13, where sea water was used, gave 63.4, 62.5, and 55.5 per cent of alcohol, respectively. The percentage yields range inversely to the concentration of the sea water used and are the result of the influence of the impurities carried by this water.

A sample of molasses was prepared as under Table VI and exposed to the air without inoculation. At the end of forty hours active fermentation had begun, due to inoculation by wild yeasts, and the sample showed an alcohol content of 1.40 per cent. The maximum alcohol content, 6.61 per cent, was shown after one hundred twenty hours had elapsed from the time of mixing.

Much interest is taken in this and other laboratories in the properties of the compound occurring in tiqui-tiqui (the polishings from rice), brewer's yeasts, wheat bran, etc., and which is known by the names vitamine, oryzanin, water soluble B, etc. Kurono [18] was led to investigate its effect on yeast in fermentation. He made an alcohol extract of rice polishings and added small quantities of the dried extract to his ferment. The extract accelerated the fermentation even more than does peptone or asparagine.

The results obtained by Kurono led us to investigate the effect of adding rice polishings directly to the ferment. These results are tabulated in Table X. Because of the poor results obtained, another sample (No. 7) was inoculated, this time from sample 6, to determine if the yeast would be more active after having become accustomed to the tiqui-tiqui.

TABLE X.—*The effect of adding varying amounts of tiqui-tiqui (rice polishing) to fermenting molasses.*

| Sample No. | Tiqui-tiqui added to 1 liter. | Alcohol. | | | | | 136 hours. | | Alcohol. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 16 hours. | 40 hours. | 64 hours. | 88 hours. | 112 hours. | Alcohol. | Acidity. | Maximum yield. | Yield, per cent of theoretical. |
| | g. | | | | | | | | | |
| 1 | 5 | 0.38 | 1.50 | 2.50 | 3.05 | 3.99 | 5.24 | 10.86 | 5.24 | 70.3 |
| 2 | 10 | 0.38 | 1.50 | 2.64 | 2.90 | 3.90 | 4.66 | 11.44 | 4.66 | 62.7 |
| 3 | 20 | 0.38 | 1.60 | 2.64 | 4.13 | 5.07 | 5.70 | 10.66 | 5.70 | 76.5 |
| 4 | [a]5 | 0.38 | 1.60 | 2.50 | 3.13 | 4.05 | 5.14 | 10.84 | 5.14 | 69.4 |
| 5 | [a]10 | 0.38 | 1.54 | 2.84 | 3.55 | 4.04 | 5.31 | 9.81 | 5.31 | 71.3 |
| 6 | [a]20 | 0.38 | 1.60 | 2.98 | 3.85 | 4.71 | 5.24 | 11.08 | 5.24 | 70.3 |
| 7 | 5 | 0.35 | 1.60 | 2.50 | 3.41 | 3.97 | 4.12 | 12.32 | 4.12 | 55.5 |

[a] Cooked.

[18] *Journn. Coll. Agr., Imp. Univ. Tokyo* (1915), 5, 305.

A comparison of the results with the results obtained when the standard solution for Table VIII was fermented shows that the addition of tiqui-tiqui has no beneficial influence. One result, sample 3, only shows a real increase in alcohol content over the sample where no yeast food was added (see sample 7, Table VIII). The acidity in every one was high at the end of the sixth day, indicating that the addition of tiqui-tiqui contaminates the solution or makes the ferment more favorable for the growth of bacteria. To extract the tiqui-tiqui with alcohol as done by Kurono would be more expensive than using ammonium sulphate. Culturing the yeast in ferment to which tiqui-tiqui has been added did not stimulate its ability to grow in the presence of tiqui-tiqui. The use of ammonium salts [19] lowers the yield of the higher alcohols (fusel oils) and is, therefore, an advantage for this reason.

Yeast can be invigorated by culture in a nourishing ferment, and such yeast acquires a vigor that induces rapid fermentation. It can be accustomed to conditions that would ordinarily inhibit its grow and that are unfavorable to the growth of bacteria and wild yeasts. Advantage has been taken of this property, in the method of fermentation known as the Molhant process, to increase the resistance of the yeast to more concentrated solutions of alcohol and to add to its ability to ferment higher concentrations of molasses. Mirior,[20] in using this method, proceeded as follows: Yeast was added to a small amount of molasses of 6° Baumé acidified with 3.5 cubic centimeters of hydrochloric acid per liter, and the whole was allowed to ferment. When fermentation was active, the ferment was pumped to a larger tank and more molasses of similar quality was added. This was permitted to ferment twenty-four hours and then put in a larger tank, where plain molasses of 14° Baumé was added until the whole mixture was about 12° Baumé. Fermentation was complete in from twenty-four to thirty hours, and a must of 9 to 9.5 per cent alcohol was obtained. The process gives 60.23 liters of alcohol per 100 kilograms of sugar, calculated as sucrose. He states that this is 1.5 liters per 100 kilograms more than is obtained by the old process.

To determine if this process would increase the yields of alcohol with the yeast at hand, the following experiments re-

[19] Ehrlich, Paul, *Ber. d. deutsch. chem Ges.* (1906), 39, 4072; (1907), 40, 1027.

[20] *Bull. Assoc. Chim. de Sucr. et Dist.* (1914), 31, 936.

corded were planned and performed; solutions were made up as described under *a*, *b*, and *c:*

*a*. Two hundred fifty cubic centimeters of 20 per cent molasses solution, plus 0.25 cubic centimeter concentrated sulphuric, plus 1 equivalent of ammonium sulphate were sterilized once by heating and inoculated with yeast. Four of these solutions were prepared and allowed to ferment.

*b*. Twenty-four hours later 250 cubic centimeters of solutions identical with *a* were added to each of the above four solutions.

*c*. Twenty-four hours later 500 cubic centimeters of quantities of solutions of the strength given below were added to the respective samples:

1. One hundred twenty grams of molasses in 500 cubic centimeters of solution plus the usual proportion of acid and ammonium sulphate.
2. One hundred thirty grams of molasses in 500 cubic centimeters of solution plus the usual proportion of acid and ammonium sulphate.
3. One hundred forty grams of molasses in 500 cubic centimeters of solution plus the usual proportion of acid and ammonium sulphate.
4. One hundred fifty grams of molasses in 500 cubic centimeters of solution plus the usual proportion of acid and ammonium sulphate.

This makes sample 1 a 22 per cent molasses solution; 2, a 23 per cent; 3, a 24 per cent; and 4, a 25 per cent.

The first sample for determination of alcohol content was taken at the end of twenty-four hours after the ferment was completed, and subsequent samples were taken at intervals of twenty-four hours, as recorded in Table XI.

TABLE XI.—*Yields of alcohol obtained from molasses by the use of the Molhant process.*

| Sample No. | Molasses. | Alcohol. | | | | 120 hours. | | 144 hours. | Alcohol. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 24 hours. | 48 hours. | 72 hours. | 96 hours. | Alcohol. | Acidity. | Alcohol. | Maximum yield. | Yield, per cent of theoretical. |
| | *P. cent.* | | | | | | | | | |
| 1 | 22 | 3.12 | 4.94 | 6.46 | 7.16 | 7.41 | 8.52 | 7.25 | 7.41 | 90.7 |
| 2 | 23 | 3.05 | 4.94 | 6.70 | 7.16 | 7.41 | 8.40 | 7.41 | 7.41 | 86.8 |
| 3 | 24 | 3.55 | 4.94 | 6.79 | 7.16 | 7.89 | 8.40 | 7.89 | 7.89 | 88.5 |
| 4 | 25 | 3.63 | 4.86 | 6.61 | 7.81 | 8.14 | 7.76 | 8.00 | 8.14 | 87.7 |

The maximum alcohol content was attained at the end of the fifth day. The percentage of alcohol yield of the theoretical for sample 1 is the highest obtained in any of the experiments carried out and would thus yield a greater revenue to the manufacturer. The highest concentrations gave a somewhat less yield of alcohol, but even they are on a par and in many cases

superior in percentage yield of alcohol to those of the preceding experiments with more dilute solutions. The length of time for the fermentation from beginning to end is two to three days longer than by the method in vogue here, but the initial solution being of smaller bulk requires less space, and the cost of the extra space would be compensated for by the greater yields of alcohol obtained. Besides, much space is at present consumed by the tardiness in distillation when the fermentation is complete. It is common practice to allow the must to stand several days after fermentation is finished. The distillers do not realize that the delay results in a loss of alcohol from evaporation and from bacterial action, more especially the latter.

In order that further data on this method might be collected from more thorough trials, the nine experiments recorded in Table XII were performed. The nine samples were first made by diluting 30 grams of the stock molasses to 200 cubic centimeters and adding the regular amount of sulphuric acid and one equivalent of ammonium sulphate. This solution stood two days until the fermentation was proceeding strongly, in the case of the first of each duplicate, while the second of each duplicate stood for only one day, and then to:

No. 1 were added 300 cubic centimeters of a solution containing 60 grams of molasses and the regular amount of acid ammonium sulphate.

No. 2's were added 300 cubic centimeters of a solution containing 70 grams of molasses and the regular amount of acid and ammonium sulphate.

No. 3's were added 300 cubic centimeters of a solution containing 80 grams of molasses and the regular amount of acid and ammonium sulphate.

No. 4's were added 300 cubic centimeters of a solution containing 80 grams of molasses and the regular amount of acid and ammonium sulphate.

No. 5's were added 300 cubic centimeters of a solution containing 90 grams of molasses and the regular amount of acid and ammonium sulphate.

On the following day the following solution was added to:

No. 1, 110 grams molasses, regular amount of acid and ammonium sulphate in 500 cubic centimeters.

No. 2's, 120 grams molasses, regular amount of acid and ammonium sulphate in 500 cubic centimeters.

No. 3's, 120 grams molasses, regular amount of acid and ammonium sulphate in 500 cubic centimeters.

No. 4's, 130 grams molasses, regular amount of acid and ammonium sulphate in 500 cubic centimeters.

No. 5's, 130 grams molasses, regular amount of acid and ammonium sulphate in 500 cubic centimeters.

This makes:

| Sample No. | Per cent molasses solution. |
|---|---|
| 1 | 20 |
| 2's | 22 |
| 3's | 23 |
| 4's | 24 |
| 5's | 25 |

One hundred cubic centimeter samples were withdrawn for the determination of the alcoholic content at twenty-four hour intervals. The results are recorded in Table XII.

TABLE XII.—*Some further data obtained by use of the Molhant process in the fermentation of molasses.*

| Sample No. | Molasses. | Alcohol. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 24 hours. | 48 hours. | 72 hours. | 96 hours. | 112 hours. | 144 hours. | Maximum yield. | Yield, per cent of theoretical. |
| | *P. cent.* | | | | | | | | |
| 1 | 20 | 3.55 | 5.79 | 6.22 | 6.81 | 6.46 | 6.15 | 6.81 | 91.1 |
| 2 | 22 | 3.74 | 5.69 | 6.54 | 7.34 | 7.16 | 6.85 | 7.34 | 89.9 |
| | | 3.13 | 4.79 | 5.69 | 6.23 | 6.95 | 7.41 | 7.41 | 90.6 |
| 3 | 23 | 3.74 | 5.99 | 6.69 | 7.39 | 7.09 | 6.91 | 7.39 | 85.7 |
| | | 2.89 | 4.71 | 5.61 | 6.15 | 6.88 | 7.16 | 7.16 | 83.9 |
| 4 | 24 | 3.55 | 6.39 | 6.59 | 7.58 | 7.58 | 6.91 | 7.58 | 85.4 |
| | | 3.13 | 5.01 | 5.76 | 6.31 | 7.32 | 7.58 | 7.58 | 85.4 |
| 5 | 25 | 4.05 | 5.99 | 6.95 | 7.65 | 8.14 | 7.65 | 8.14 | 87.7 |
| | | 2.78 | 4.94 | 5.84 | 6.46 | 7.42 | 8.06 | 8.06 | 84.9 |

The 20 per cent solutions by the Molhant process have a yield equal to the maximum obtained by the regular method. The results for high concentrations up to 25 per cent molasses solutions are uniformly good. In every case they are above 80 per cent, the percentage yield that is considered good distillery practice. In fact, the average percentage yields are higher than 85 in each case, and the consistence of the results and the simplicity of the process make it a valuable method. In the distilleries using nipa juice and molasses the custom of mixing nipa juice with molasses solution in making up the ferment is followed. This is a modified Molhant process, where the nipa juice carries the yeast. Such mixtures usually give excellent results in the early part of the nipa-juice season, but after the middle of the season yields from such mixtures decrease and often become so bad that the use of nipa juice must be discontinued. An investigation [21] by the Bureau of Science shows that the loss of the

[21] Pratt, D. S., et al., *This Journal, Sec. A* (1913), **8**, 377.

sugar content of nipa juice is due to the activity of a peroxidase elaborated by the flower stalk. This enzyme is not produced by long stems to any extent, but as the stems become short, due to repeated cutting from the end to renew the flow of juice, the quantity of peroxidase elaborated becomes large, and any delay in heating or adding sulphites will result in the loss of much or all of the sugar present in the original juice. Where the juice is mixed with molasses solution much of the sugar of the molasses is also destroyed by the enzyme. Sterilization would destroy the enzyme, but this would likewise destroy the yeast present in the nipa juice and would prevent the inoculation of the ferment by means of the nipa juice, which is one of the reasons for adding it to the diluted molasses.

A summary of the results obtained by use of the Molhant process is included.

TABLE XIII.—*Average yield of alcohol by use of the Molhant process.*

| Molasses. | Number of samples run. | Yield. | | |
|---|---|---|---|---|
| | | Average, per cent of theoretical. | Maximum. | Minimum. |
| *Per cent.* | | | | |
| 20 | 1 | 91.1 | ---------- | ---------- |
| 22 | 3 | 90.4 | 90.7 | 89.9 |
| 23 | 3 | 85.5 | 86.8 | 83.9 |
| 24 | 3 | 86.4 | 88.5 | 85.4 |
| 25 | 3 | 86.8 | 87.7 | 84.9 |

Table XII shows that the more concentrated solutions gave high yields of alcohol and that the use of the process will result in the saving of fermenting space; fuel for distillation, since more concentrated solutions of alcohol will be obtained; and the production of dependable high yields of alcohol.

A sample of ferment, 20 per cent molasses with the regular amount of sulphuric acid and 1 equivalent of ammonium sulphate, was added and inoculated with yeast, and the temperature was kept at 25° C. to demonstrate the effect of lower temperatures. The results are given in Table XIV.

The sample gave a yield of 91.1 per cent of the theoretical amount of alcohol obtainable. This result illustrates the advantage of keeping the ferment as free as possible from bacterial contamination. Temperatures below 30° C., together with vigorous yeast growth, accomplished this end.

TABLE XIV.—*Results obtained for a 20 per cent solution of molasses fermented at a temperature of 25°.*

| Sample No. | Alcohol. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 16 hours. | 40 hours. | 64 hours. | 88 hours. | 112 hours. | 136 hours. | Maximum yield. | Yield, per cent of theoretical. |
| 1 | 0.99 | 3.69 | 5.24 | 6.69 | 6.77 | 6.70 | 6.77 | 91.1 |

The next experiment was a repetition of the preceding on a larger scale. A 50-gallon barrel was cleaned and fitted with a coil, 150 liters of a 22 per cent solution of molasses were placed in the barrel, 300 grams of sulphuric acid and 30 grams of ammonium sulphate were added, and the whole was heated by passing high pressure steam through the coil. Then water was passed through the coil, the contents of the barrel were inoculated with 2 liters of yeast ferment when the temperature had been lowered to 30° C., and the whole well mixed and allowed to ferment. The temperature of the solution even during the active period of fermentation never rose above 29° C.

TABLE XV.—*Results of the fermentation of 150 liters of 20 per cent molasses solution at a temperature below 30° C.*

| Sample No. | Alcohol. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 16 hours. | 40 hours. | 64 hours. | 88 hours. | 112 hours. | 136 hours. | Maximum yield. | Yield, per cent of theoretical. |
| 1 | 0.91 | 3.34 | 4.94 | 5.85 | 7.16 | 7.34 | 7.34 | 89.8 |

The yield of alcohol is well above 80 per cent, the yield of good distillery practice.

With the exception of the preceding test, where an oil barrel was used, all the experiments were carried out in glass bottles. In order to test our conclusions in a more practical way and to meet the possible accusation that such yields would be impossible under distillery conditions, permission was obtained to run control tests at one of the distilleries of the Islands.

A vat of about 15,000 liters' capacity was fitted with a coil having a surface area of about 7.5 square meters, and connections were made by which water from the river or exhaust steam from the engines could be circulated through the coil.

Three thousand three hundred thirty-five kilograms of molasses were placed in this vat, and the volume was increased to 14,000 liters by the addition of warm condenser water. Steam was passed through the coil, until the temperature of the ferment reached 70° C. Then cooling water having a temperature of 28° was passed through the coil. Because of the inadequate size of the coil, these operations were extended over a period of more than forty hours. The same proportion of concentrated sulphuric acid (2 grams per liter of ferment) was added, but instead of one equivalent of ammonium sulphate, two were added (0.4 gram per liter of ferment), or double the amount used in the preceding experiment was used to increase the rate of fermentation. One hundred fifty liters of inoculating solution were then added, and the fermentation was allowed to proceed.

The molasses employed was different from that used in all of the previous work described in this article, as it had been diluted to facilitate its removal from the containing tanks.

TABLE XVI.—*Data on molasses used in fermentation experiment tabulated in Tables XVIII to XXIV.*

| Table. | Molasses. | | Dry substance in molasses. | | Sugar as glucose in dry substance. | Glucose introduced. |
|---|---|---|---|---|---|---|
| | *Liters.* | *Kilos.* | *Per cent.* | *Kilos.* | *Per cent.* | *Kilos.* |
| XVIII | 2,500 | 3,335 | 71.0 | 2,369 | 78.0 | 1,848 |
| XX | 2,181 | 3,032 | 72.6 | 2,201 | 79.8 | 1,756 |
| XXII | 2,500 | 3,335 | 71.0 | 2,369 | 78.1 | 1,850 |
| XXIV | 2,700 | 3,676 | 71.0 | 2,610 | 78.0 | 2,033 |

TABLE XVII.—*Data on ferment, results of which are recorded in Table XVIII.*

| | Liters. |
|---|---|
| Water | 11,600 |
| Molasses | 2,500 |
| Inoculating solution | 150 |
| Total initial volume | 14,250 |
| Final volume | 14,000 |

NOTE.—Sulphuric acid, 2 grams per liter; ammonium sulphate, 0.4 gram per liter; initial brix, 16.5.

The yield in Table XVIII is very flattering indeed, and when compared with some of the results obtained in the local distilleries, the differences are striking.

A second control test was run (Table XIX).

TABLE XVIII.—*Results of fermenting molasses on a large scale with temperature control.*

| Fermentation. | Temperature. | Cell count. | Alcohol, by volume. | Density, degree brix. | Alcohol. | |
|---|---|---|---|---|---|---|
| | | | | | Maximum yield. | Yield, per cent of theoretical. |
| *Hours.* | °C. | | | | | |
| 24 | 30 | 10.6 | 2.98 | [a]12.2 | | |
| 48 | 33 | 120.0 | 5.91 | 6.4 | | |
| 72 | 30 | 76.0 | 7.01 | 4.2 | | |
| 96 | 31 | 71.0 | 7.25 | 3.9 | 7.25 | 89.8 |
| 120 | 29 | 63.0 | 7.16 | 3.8 | | |
| 136 | 28 | 47.0 | 6.92 | 3.8 | | |

[a] Original density, 16.5 brix.

TABLE XIX.—*Data on ferment, results of which are recorded in Table XX.*

| | Liters. |
|---|---|
| Water | 12,021 |
| Molasses | 2,181 |
| Inoculating solution | 150 |
| Total initial volume | 14,350 |
| Total final volume | 14,150 |

NOTE.—Sulphuric acid, 2 grams per liter; ammonium sulphate, 0.4 gram per liter; initial brix, 16.5.

TABLE XX.—*Results of second trial of fermenting molasses with temperature control.*

| Fermentation. | Temperature. | Cell count. | Alcohol, by volume. | Density. | Alcohol. | |
|---|---|---|---|---|---|---|
| | | | | | Maximum yield. | Yield, per cent of theoretical. |
| *Hours.* | °C. | | | | | |
| 16 | 33 | 35 | | 16.3 | | |
| 40 | 33 | 90 | 3.84 | 9.7 | | |
| 64 | 31.5 | 80 | 6.27 | 4.9 | | |
| 88 | 31 | 76 | 6.81 | 3.8 | 6.81 | 90.7? |
| 112 | 30 | 72 | 6.69 | 3.7 | | |

This result is very slightly superior to that of Table XVIII and shows that consistent yields can be procured by exercising the precautions used in these two experiments.

A control test in an adjoining vat was run to determine the yield under present distillery methods. This vat had no cooling coil, and the ferment was not inoculated.

TABLE XXI.—*Data on ferment, results of which are recorded in Table XXII.*

| | Liters. |
|---|---|
| Water | 12,600 |
| Molasses | 2,500 |
| Total initial volume | 15,100 |
| Total final volume | 14,950 |

NOTE.—Sulphuric acid, 2 grams per liter; ammonium sulphate, 0.4 gram per liter; initial brix, 16.2.

TABLE XXII.—*Results obtained by fermentation of molasses without inoculation and without cooling coil.*

| Fermentation. | Temperature. | Cell count. | Alcohol, by volume. | Density. | Alcohol. | |
|---|---|---|---|---|---|---|
| | | | | | Maximum yield. | Yield, per cent of theoretical. |
| *Hours.* | °*C.* | | | | | |
| 16 | 31 | 1.3 | ---------- | 16.2 | ---------- | ---------- |
| 40 | 38 | 78.7 | 8.76 | 9.4 | ---------- | ---------- |
| 64 | 38 | 56.7 | 5.16 | 6.8 | ---------- | ---------- |
| 88 | 34 | 47.9 | 5.24 | 6.4 | 5.24 | 70.1 |
| 112 | 32 | 41.0 | 4.86 | 6.4 | ---------- | ---------- |

The yield recorded in Table XXII is only 77.9 per cent of what the yield was in Table XVIII. This excess of Table XVIII over Table XXII can be ascribed to the one sterilization at the beginning, to the use of pure yeast cultures, and to the reduced temperature during fermentation. The high temperature in the latter case is conducive to bacterial growth, greater evaporation of the alcohol, increase of acidity, and incomplete fermentation, because of the decreased production of enzymes from the yeast. The attenuation, which is an approximate measure of the degree of alcoholic fermentation, was not as complete in Table XXII, where it proceeded from 16.2 to 6.4, as it was in Table XVIII, where it went from 16.5 to 3.8.

As has been already mentioned, many of the distilleries of the Philippine Islands ferment nipa juice either alone or mixed with diluted molasses. In order that the efficiency of this method might be determined, the experiment tabulated in Table XXIII was carried out.

TABLE XXIII.—*Constitution of ferment, results of which are recorded in Table XXIV.*

| | Liters. |
|---|---|
| Water | 10,000 |
| Tuba | 8,700 |
| Molasses | 2,700 |
| Total initial volume | 21,400 |
| Total final volume | 21,000 |

NOTE.—Initial acidity, 8.5 cubic centimeters 0.1 *N* alkali in 10 cubic centimeters of ferment; initial brix, 12.6.

TABLE XXIV.—*Results for a mixture of tuba and molasses.*

| Fermentation. | Temperature. | Cell count. | Alcohol by volume. | Density. | Acidity. | Alcohol. | |
|---|---|---|---|---|---|---|---|
| | | | | | | Maximum yield. | Yield, per cent of theoretical. |
| *Hours.* | °*C.* | | | | | | |
| 16 | 42 | 74 | 5.09 | 7.4 | 10 | ---------- | ---------- |
| 40 | 40 | 54 | 5.61 | 5.9 | 10 | 5.61 | [a] 66.7 |
| 64 | 37 | 50 | 5.54 | 5.8 | 11 | ---------- | ---------- |
| 88 | 35 | 48 | 5.46 | 5.7 | 14.5 | ---------- | ---------- |
| 112 | 33 | 43 | ---------- | 5.5 | 16.5 | ---------- | ---------- |

[a] Assuming that the sugar content is 10 per cent, which is less than good tuba should contain.

The yield recorded in Table XXIV was somewhat less than in the preceding test and is not comparable with the yield obtained in fermenting a solution in which the temperature is kept below 30° C. and vigorous clean yeast is used for inoculation. The acidity of this solution increased rapidly at first, doubtless owing to the activity of the peroxidase carried in the tuba. The activity of the peroxidase will decline when the alcohol content of the ferment increases, and this period is marked by the period of no change in the acidity of the ferment, but after a short interval it again increases, due to the activity of bacteria.

The density, as shown in Tables XXII and XXIV, has not decreased to the same extent as in Tables XVIII and XX. Many results better than these recorded in Tables XXII and XXIV are obtained by the distilleries of the Islands. The distillery to which we had access has records of better yields than these, but the fact that such yields occur when the "tuba has gone bad," or because of other reasons, shows the need for closer supervision and greater knowledge of the best conditions for fermenting this molasses.

## RECOMMENDATIONS

We recommend the sterilization of the molasses solution wherever this can be attained without too great cost or the installation of extra machinery. If this is impossible, the use of good water for diluting the molasses to a definite density, about 16.5 brix, is essential. Two grams of sulphuric acid and at least 0.4 gram of ammonium sulphate to every liter of ferment should be added. Inoculate the ferment with clean yeast. One part of fermenting wort to 100 or 150 parts of ferment is the right proportion. Seed for the production of this inoculation

yeast can be obtained from the Bureau of Science, and at the same time instruction can be procured for keeping this comparatively free from infection. Clean yeast can be obtained by inoculating a small quantity of sterilized 10 per cent molasses wort by means of a sterile platinum wire or by the addition of a few drops of stock yeast. When this is fermenting strongly, it should be added to a larger volume of sterile molasses solution (12 brix), preserving the proportion of 1 to 100 (or 150), and the operation can be repeated with this volume until the content of yeast is sufficient to inoculate the vat, which is ready to be fermented. If care is exercised in choosing ferment in which the yeast is not badly contaminated, the new vats can be inoculated by the addition of stock solution from vats in active fermentation. By beginning with a 10 per cent solution of molasses and making each successive solution slightly more concentrated until a brix of 16.5 is attained, the ability of the yeast to ferment in more highly concentrated solutions is strengthened. In other words, the principles embodied in the Molhant process are being put in operation. The point of maximum alcohol content should be determined by frequent determinations of the alcohol present in the fermenting solution. When this point is reached, the ferment should be distilled without unnecessary delay. The ebullioscope is used by some concerns for this determination, but its use is unsatisfactory and cannot be relied upon. The manufacturers specifically say it is for use in determining the alcohol content of dilute alcohol solutions, dry wines, etc. Where sugar or other solid is present in solution, the results obtained by it are unreliable; consequently the alcohol content of fermenting molasses cannot be measured by this instrument. The temperature of the ferment should be kept between 28° and 30° C. by suitable cooling coils.

## SUMMARY

Some statistics of the alcohol industry in the Philippine Islands and abroad are given.

The data of a number of experiments with fermenting molasses are recorded. These show the influence of various salts on the rate of fermentation, the yield of alcohol, and the virility of the yeast. They include several trial experiments on a large scale with and without temperature control.

Certain recommendations are made for the improvement of the present methods of fermenting molasses.

# THE RADIOACTIVITY OF THE WATERS OF THE MOUNTAINOUS REGION OF NORTHERN LUZON [1]

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ONE PLATE AND TWO TEXT FIGURES

In a previous paper [2] the results of a series of measurements of the radioactivity of typical Philippine waters were reported. About 90 waters were examined, including 44 from springs in the mountainous region of northern Luzon. This province is, in the main, a volcanic region, of which the—

> Geology clearly indicates, geologically speaking, the evidence of only recent vulcanism.[3]

It contains an abundance and a variety of springs, many of them hot and heavily mineralized; hence it is an especially desirable place for work of this kind.

In the work referred to, there was no apparent relation to be deduced between the radioactivity of the waters and the chemical quality of the geological formations from which they were derived. The work done was admittedly preliminary in character, and the result could not be considered conclusive.

With the exception of certain sources in Ifugao subprovince, the springs examined in Mountain Province were uniformly low in radium emanation content. There was no apparent reason for this peculiarity, as the waters studied were from many different geological formations and showed great variation in chemical quality.

It seemed of possible significance that the only strongly radioactive waters were encountered in Kiangan and Banaue, the only places east of Polis Range at which we had made examinations. However, the available time and the exigencies of mountain travel did not permit more extensive investigation. Recently it has been found possible to extend the work, with the results set forth in this paper.

In addition to the places mentioned in the preceding report, the accompanying map (fig. 1) shows the following places at

[1] Received for publication July, 1917.

[2] Wright, J. R., and Heise, G. W., The radioactivity of Philippine waters, *This Journal, Sec. A* (1917), 12, 145.

[3] Eveland, A. J., Notes on the geology and geography of the Baguio mineral district, *ibid.* (1907), 2, 207–233.

which work was done this year: Noso, Aritao, Bambang, Bayombong, Solano, Bagabag, Salinas, and San Luis, Nueve Vizcaya; Amdangle, Banaue, Sapao, Aoua, and Monhuyhuy, in Ifugao, Mountain Province; and Loo, Buguias, Lutab, Daklan Ambuklao, and Baguio in Benguet, Mountain Province.

In addition to the regular equipment used for the determina-

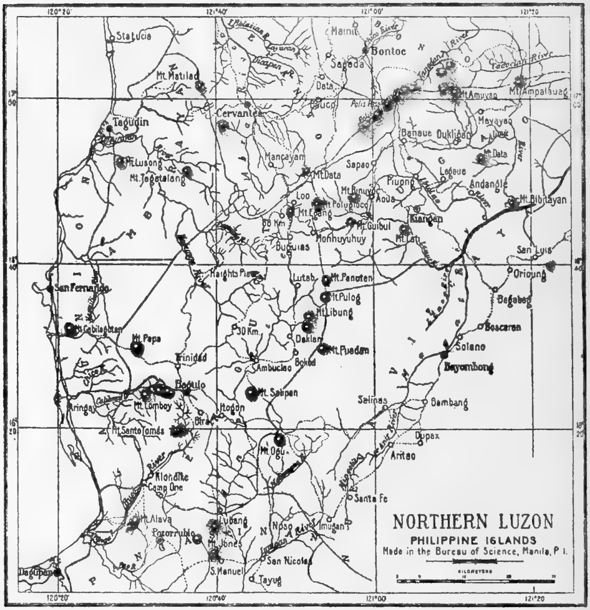


FIG. 1. A part of northern Luzon.

tion of radioactivity, we took with us a small chemical field laboratory, modified to meet the unusually severe conditions of mountain travel. The use of this laboratory not only enabled us to obtain data of interest in the study of radioactivity, but it was also of definite value in furthering the field survey [4] of Philippine water supplies now carried on by the Bureau of Science.

[4] Heise, G. W., Water supplies in the Philippine Islands, II, ibid. (1915), 10, 137.

Except that a Schocky-Willis radioscope was used instead of the Spindler-Hoyer electroscope, apparatus and method were essentially the same as those previously described in detail.[5] Because of the great bulk of the Schocky-Willis apparatus and its complete lack of accessories for field work, a smaller brass ionization chamber was constructed in the Bureau of Science. The collecting cans and other necessary field equipment from the Spindler and Hoyer outfit were added before the apparatus was taken into the field. By cutting down the size of the ionization chamber, the sensitiveness was reduced approximately to 40 per cent that of the Spindler and Hoyer electroscope. This lack of sensitiveness, together with the mediocrity of the telescope and the difficulty in the field of getting readings with the leaf charged to the same potential, made readings somewhat uncertain and increased the percentage of error. Check determinations made it appear probable, however, that the limits of error mentioned previously had not been greatly exceeded. The results obtained may be, therefore, considered reliable, except for waters of low activity, for which the exact value of the emanation content is of minor significance.

The modified apparatus, as assembled in the field for a determination of radioactivity, is shown in Plate I.

As before, no attempt was made to determine anything but radium emanation content. The data secured for the radioactivity of the waters of northern Luzon are shown in Table I, the results obtained in 1916 and already reported[5] being included to enable the presentation of the work as a whole.

TABLE I.—*Radioactivity of waters of northern Luzon.*

| No. | Date tested. | Location (province, subprovince, and town or district). | Source. | Elevation above sea level. | Temperature. | Radium emanation per liter as grams Ra × $10^{-12}$. |
|---|---|---|---|---|---|---|
| | | MOUNTAIN PROVINCE. | | *Meters.* | °C. | |
| 1 | May 31, 1916 | Amburayan, Tagudin | Flowing well near cemetery. | ?10 | ?32 | 341 |
| 2 | do | do | Flowing well, plaza | ?10 | 32 | trace |
| 3 | do | do | Flowing well near school | ?10 | 37 | 137 |
| 4 | May 24, 1917 | Benguet, Ambuklao | North spring | 660 | 27 | trace |
| 5 | do | do | West spring | 660 | 26 | 60 |
| 6 | May 1, 1916 | Benguet, Baguio | Antimok River spring * | 1,300 | (a) | 0 |

[a] Nonthermal.

* Waters which, owing to the nature of the source, could not be obtained just as they emerged from the ground, or those which may not have been typical ground waters owing to their derivation from springs believed to be local or temporary.

[5] Wright and Heise, loc. cit.

TABLE I.—*Radioactivity of waters of northern Luzon*—Continued.

| No. | Date tested. | Location (province, subprovince, and town or district). | Source. | Elevation above sea level. | Temperature. | Radium emanation per liter as grams Ra × $10^{-12}$. |
|---|---|---|---|---|---|---|
| | | | | *Meters.* | °*C.* | |
| 7 | April 29, 1916 | Benguet, Baguio | Camp John Hay, Cariño spring. | ?1,300 | (a) | 194 |
| 8 | do | do | Camp John Hay, ice plant spring. | 1,450 | (a) | 122 |
| 9 | April 27, 1916 | do | City spring, Bokawkan Road. | 1,400 | (a) | 107 |
| 10 | May 27, 1916 | do | Consolidated Mine spring. | 985 | 28 | 93 |
| 11 | May 26, 1916 | do | Dominican Home spring * | 1,350 | 20 | 111 |
| 12 | April 28, 1916 | do | Federle's Spring, Suyoc Trail. | 1,650 | (a) | 137 |
| 13 | April 26, 1916 | do | Government Center spring. | 1,350 | 22 | 163 |
| 14 | May 29, 1917 | do | Small spring, adjacent to No. 13. | 1,350 | 22 | 200 |
| 15 | May 1, 1916 | do | Headwaters Mine spring. * | 1,150 | 21 | 0 |
| 16 | April 27, 1916 | do | Sanitary Camp spring | 1,400 | (a) | 29 |
| 17 | April 28, 1916 | do | Pakdal spring | 1,400 | (a) | trace |
| 18 | May 28, 1916 | do | Spring at slide, Bua Road. * | 1,400 | 23 | 70 |
| 19 | May 19, 1917 | Benguet, Buguias | Salt spring near presidencia. | 1,400 | 60 | 0 |
| 20 | do | do | Salt spring, south of presidencia. | 1,400 | 57 | 0 |
| 21 | May 20, 1917 | do | Warm spring across river | 1,400 | 48 | 0 |
| 22 | do | do | Warm spring near No. 21 | 1,375 | 45 | trace |
| 23 | May 23, 1917 | Benguet, Daklan | Asin (salt) spring | 900 | 52 | 95 |
| 24 | do | do | Badukbuk solfatara | 1,350 | ?70 | (b) |
| 25 | do | do | Kakomotan spring | ?1,300 | 22 | 0 |
| 26 | do | do | Palungod spring | 1,100 | 25 | 270 |
| 27 | May 5, 1916 | Benguet, Haight's | Spring near house* | 2,550 | (a) | 0 |
| 28 | do | do | Spring near barn* | 2,550 | (a) | 0 |
| 29 | Dec., 1916 | Benguet, Itogan | Itogon hot spring | ?1,150 | ?60 | 0 |
| 30 | May 29, 1916 | Benguet, Klondike | Hot spring | 180 | ?55 | trace |
| 31 | May 22, 1916 | Benguet, Loo | Rest house spring | 1,800 | (a) | trace |
| 32 | Dec., 1916 | Benguet, Lubong | Hot spring | ?50 | ?200 | 0 |
| 33 | May 21, 1917 | Benguet, Lutab | Duakan spring | 1,200 | 22 | 0 |
| 34 | do | do | Roadside spring, Kabayan. | 1,150 | 20 | 130 |
| 35 | do | do | Ubud spring | 1,100 | 21 | 140 |
| 36 | May 4, 1916 | Benguet, Mountain Trail, Kilometer 30. | Spring near rest house * | 1,770 | (a) | 0 |
| 37 | do | do | Spring on Atols Trail * | 1,750 | (a) | 0 |
| 38 | May 7, 1916 | Benguet, Mountain Trail, Kilometer 80. | Spring near rest house * | 2,200 | (a) | 0 |

[a] Nonthermal.

[b] Emanation was high; sample of gas bubbling through a pool of hot water.

* Water which, owing to the nature of the source, could not be obtained just as they emerged from the ground, or those which may not have been typical ground waters owing to their derivation from springs believed to be local or temporary.

TABLE I.—*Radioactivity of waters of northern Luzon*—Continued.

| No. | Date tested. | Location (province, subprovince, and town or district). | Source. | Elevation above sea level. | Temperature. | Radium emanation per liter as grams Ra × $10^{-12}$. |
|---|---|---|---|---|---|---|
| | | | | *Meters.* | °C. | |
| 39 | Dec., 1916 | Benguet, Trinidad | Spring near municipio | 1,250 | [a]21 | 0 |
| 39 | May 14, 1916 | Bontoc, Bontoc | City spring | 920 | ([a]) | trace |
| 40 | do | do | Spring near city stables | 920 | ([a]) | trace |
| 41 | May 13, 1916 | do | 2 springs, barrio Samoki * | 920 | ([a]) | 0 |
| 42 | May 15, 1916 | Bontoc, Mainit | Mainit (hot) salt spring | 1,300 | 100 | 0 |
| 43 | May 11, 1916 | Bontoc, Sagada | Mission spring | 1,650 | ([a]) | 111 |
| 44 | do | do | Underground river | 1,450 | ([a]) | trace |
| 45 | May 12, 1616 | do | Spring, barrio Tetepan | 1,750 | ([a]) | 0 |
| 46 | do | do | Spring at slide, Tetepan | 1,300 | ([a]) | 263 |
| 47 | May 9, 1916 | Lepanto, Cervantes | Municipal supply | ?1,000 | ([a]) | 0 |
| 48 | May 10, 1916 | do | Hot spring, river bank | 770 | | 0 |
| 49 | May 9, 1916 | do | Comilias hot spring | 500 | | 0 |
| 50 | May 20, 1916 | Ifugao, Aoua | Spring at Kilometer 65 | 1,300 | ([a]) | trace |
| 51 | do | do | Spring at Kilometer 76 * | 1,300 | ([a]) | 0 |
| 52 | May 17, 1916 | Ifugao, Banaue | Bognakan spring | 1,150 | 23 | 381 |
| 53 | May 16, 1917 | do | Kiakop spring | 1,300 | ([a]) | 650 |
| 54 | do | do | Magabon spring | 1,150 | ([a]) | 420 |
| 55 | May 17, 1916 | do | Paypayan spring | 1,150 | 21 | 289 |
| 56 | May 12, 1917 | Ifugao, Kiangan | Adhang spring | 1,000 | 20 | 1,200 |
| 57 | May 13, 1917 | do | Adukpung spring | 850 | 25 | 1,325 |
| 58 | do | do | Adungbu spring | 850 | 25 | 720 |
| 59 | May 18, 1916 | do | Atuda spring | 1,100 | 22 | 139 |
| 60 | May 12, 1917 | do | Lakdo spring * | 1,150 | 22 | 190 |
| 61 | May 19, 1916 | do | Malpao springs (2) | 850 | 23 | 150 |
| 62 | May 19, 1917 | do | Lubungan spring | 850 | 24 | 945 |
| 63 | May 17, 1916 | do | Piko spring * | 850 | | 1,058 |
| 64 | May 11, 1917 | do | Piko spring | 850 | 23 | 900 |
| 65 | May 17, 1917 | Ifugao, Sapao | Bolanan spring | | 23 | 175 |
| 66 | May 8, 1916 | Lepanto, Mancayan | Spring, Balili trail | 1,580 | ([a]) | 114 |
| | | NUEVA VIZCAYA PROVINCE. | | | | |
| 67 | May 7, 1917 | Bagabag | Baños spring | 300 | 26 | 130 |
| 68 | do | do | Small pump well | 300 | 27 | 130 |
| 69 | May 5, 1917 | Bambang | do | 300 | 27 | 190 |
| 70 | May 6, 1917 | Bayombong | Bangan spring | 350 | 27 | 130 |
| 71 | do | do | Plaza pump well | 300 | 26 | 130 |
| 72 | May 7, 1917 | Boscaran | Spring near school | 300 | 26 | 325 |
| 73 | May 1, 1917 | Noso | Spring near rest house | 550 | 24 | 0 |
| 74 | May 9, 1917 | Orcoring | Spring near road | (?) | 30 | 130 |
| 75 | May 4, 1917 | Salinas | Salinas salt spring | 500 | 31 | 95 |
| 76 | May 8, 1917 | San Luis | Spring in quarry | (?) | 27 | 60 |
| 77 | May 3, 1917 | Santa Fe | Santa Fe spring | 500 | 22 | 480 |
| 78 | May 6, 1917 | Solano | Solano spring | 300 | 27 | 195 |
| 79 | do | do | Solano pump well | 300 | 27 | 240 |

[a] Nonthermal.

* Water which, owing to the nature of the source, could not be obtained just as they emerged from the ground, or those which may not have been typical ground waters owing to their derivation from springs believed to be local or temporary.

The table is self-explanatory, for the most part, but there are a few points in connection with it that merit attention.

The springs in the list are typical and are representative of the country in which the work was done. They comprise the prominent and better known sources along the route of travel, among them several used for salt manufacture (Salinas, Mainit) and several hot mineral springs with reputations for medicinal virtues (Itogon, Mainit, Comilias).

The highest activity recorded ($1,325 \times 10^{-12}$) was found in Adukpung spring,[6] in Kiangan.

It will be noted that Piko spring, in Kiangan, was examined both in 1916 and 1917 and that there is a marked discrepancy between the two determinations. This difference does not necessarily indicate a variation in emanation content, nor even a serious error in the determinations, as the water from the spring in question flows into a small, covered reservoir before it is allowed to emerge; therefore a sample cannot be secured directly at the point of emergence.

As might be expected in a volcanic region, there are a number of solfataras in the area under discussion, notably at Bolotoc, at Daklan, and near Monhuyhuy. The one at Daklan, which we visited this year, is characterized by a number of vents, from which hot gases and vapors emerge, principally hydrogen sulphide, sulphur dioxide, and steam. We were unable to find any springs at this place. There were a number of excavations in which surface run-off and perhaps condensed steam had collected, forming great caldrons of hot water, some of them used as baths through which the gases and vapors bubbled. There were also a number of hot mud "springs," where the gases broke through semiliquid mud with the peculiar sound from which the solfatara presumably has derived its Igorot names (Barutbarut, Badukbuk). As the waters in the excavations just mentioned were probably surface run-off, and as they were constantly aërated by the gases bubbling through them, their activity was

[6] This spring is peculiar. It is located in the wall of a rice paddy and emerges at a level only a few decimeters below that of the water in the field. As it is separated from the rice-paddy water by less than 5 decimeters of earth, this spring looks like a mere seepage. We were assured, however, that it is a true spring, whose flow does not fail throughout the year, even during the months when the rice field is quite dry. Analysis of the water in the rice paddy showed marked differences from that from the spring, and the determination of activity seems to furnish further proof that the source is a real spring.

of minor interest. A collecting can, full of the gas taken from one of the excavations by downward displacement of water, proved to be radioactive, as indicated in Table I.

For completeness, I have compiled the available chemical data on the waters studied and have included them in Table II. All of the waters tested for radioactivity in 1917 were analyzed at the source by Mr. A. S. Behrman, chemist of this Bureau, who accompanied me on the field trip. In the case of highly mineralized waters, or when additional gravimetric determinations were desired, samples were taken to Manila in glass-stoppered bottles and analyzed in the laboratory. It should be noted that the data given under "total hardness" were obtained by a modification of the Blacher [7] potassium palmitate method and represent combined calcium and magnesium content.

Of the numerous salt springs examined, none showed more than small amounts of activity. The hot springs, too, were only slightly or not at all radioactive. These results are in agreement with those obtained elsewhere [8] and are to be expected from the low solubility of radium emanation in hot water or concentrated salt solutions. A number of waters low in radioactivity are also low in dissolved mineral matter. This is probably of little significance, except to show that certain sources, instead of being deep-seated springs, were but little more than seepage water, percolating the soil for comparatively short distances. It might be pointed out that the most radioactive waters encountered were high in calcium and magnesium content, indicating an origin in calcareous material. The work done in the Philippines up to the present time is still insufficient to justify conclusions, so that the cases noted should be regarded as isolated observations, at least for the present. However, it is worthy of note that this peculiarity is distinctly at variance with the usual observation [9] that the water from igneous rocks

[7] Blacher C., Grünberg, P., and Kissa, M., Die Verwendung von Kaliumpalmität bei der Wasseranalyse, *Chem. Zeitg.* (1913), **73**, 56–8. This method has been adapted to field work by Mr. A. S. Behrman and now forms one of the regular routine determinations in the Bureau of Science field assay of water.

[8] cf. von Höfer, H., Radioactive springs, *Intern. Zeitschr. Wasserversorgung* (1914), **1**, 52–5, 90–3; through *Chem. Abst.* (1915), **9**, 1714.

[9] cf. Clarke, F. W., Data of geochemistry, *Bull. U. S. Geol. Surv.* (1916), **616**, 315. Sahlbom, N., *Arkiv. Kemi. Min. Geol.* (1915), **6**, No. 3, 1–52; through *Chem. Abst.* (1916), **10**, 1134.

TABLE II.—*Chemical analyses of the waters tested for radioactivity.*

[Results expressed as parts per million, except as noted.]

| Location (province, subprovince, and town or district). | Source. | Capacity per minute. | Alkalinity ($CaCO_3$). | Acidity (as $CO_2$). | Iron (Fe). | Chlorides (Cl). | Carbonates (as $Na_2CO_3$) | Bicarbonates ($HCO_3$). | Sulphates ($SO_4$). | Hardness (as $CaCO_3$). |
|---|---|---|---|---|---|---|---|---|---|---|
| MOUNTAIN PROVINCE. | | *Liters.* | | | | | | | | |
| Amburayan, Tagudin [a] | Plaza artesian well | | 100.0 | nil | nil | 400.0 | 70 | 40.0 | nil | |
| Benguet, Ambuklao | North spring | 5 | 57.0 | 21.0 | 0.13 | 2.5 | nil | 69.5 | 88.8 | 86.0 |
| Do | West spring | 20 | 48.0 | 15.0 | 0.07 | 2.8 | nil | 58.6 | 73.2 | 82.0 |
| Benguet, Baguio | Camp John Hay (cariño) spring | >100 | 7.0 | 12.0 | nil | <4.0 | nil | <9.0 | trace | |
| Do | City spring | >100 | 67.0 | 1.5 | trace | 5.0 | nil | 84.0 | trace | |
| Do | Consolidated spring | 60 | 52.0 | 13.0 | 1.5 | 6.3 | nil | 63.4 | 456.0 | >400 |
| Do | Dominican home spring | >20 | 60.0 | 14.0 | 0.07 | 2.5 | nil | 73.2 | trace | 40.0 |
| Do | Federle's spring | 20 | 60.0 | 16.0 | nil | 3.3 | nil | 73.2 | trace | 40.0 |
| Do | Government Center spring | >100 | 3.0 | 14 | nil | <7.6 | nil | 4.0 | 15.0 | |
| Do | Spring adjacent to above | 60 | <5.0 | 22.0 | 0.07 | <2.5 | nil | <6.1 | 19.2 | <10.0 |
| Do | Headwaters spring | 20 | 95.0 | <5.0 | 0.13 | 3.1 | nil | 115.9 | 36.0 | 80.0 |
| Do | Pakdal spring | >20 | 110.0 | 2.5 | nil | | nil | 140.0 | trace | |
| Do | Sanitary camp spring | 10 | 13.0 | 1.5 | trace | 5.0 | nil | 160.0 | trace | |
| Do | Spring at slide, Bua Road | 25 | 8.3 | 4.8 | 0.07 | 2.5 | nil | 10.1 | trace | <10.0 |
| Benguet, Buguias [b] | Salt spring | 40 | 580.0 | 58.0 | 0.7 | 5,000.0 | nil | 708.0 | 270.0 | |
| Do | Warm spring across river | 60 | 51.0 | nil | nil | 12.5 | trace | 62.2 | 324.0 | 155.0 |
| Benguet, Buguias | Warm srping (below preceding) | 100 | 56.0 | <1.5 | nil | 17.0 | nil | 68.3 | 324.0 | 160.0 |
| Benguet, Daklan | Asin spring | small | 310.0 | 100.0 | 2.0 | 4,700.0 | nil | 378.0 | 78.0 | 950.0 |
| Do. [c] | Badukbuk | | | 2,900.0 | 450.0 | 420.0 | nil | | 3,000.0 | 700.0 |
| Do | Kakomotan spring | 10 | 100.0 | 7.0 | 0.07 | <2.5 | nil | 122.0 | nil | 66.0 |
| Do | Palungod spring | 5 | 100.0 | 18.0 | 0.13 | <2.5 | nil | 122.0 | trace | 58.0 |

[a] Total solids, 786; silica, 20; calcium, 8; magnesium, trace.

[b] Total solids, 10,800; silica, 130; aluminium (Al), 5.8; calcium (Ca), 400; magnesium, 90.

[c] Color, 200; turbidity, 5,600; total solids, 4,600; silica, 400; aluminium (Al), 205; calcium (Ca), 32; magnesium (Mg), 40.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Benguet, Itogon [d] | Hot spring | | 370.0 | nil | 12.8 | 650.0 | 37 | 410.0 | 350.0 | 560.0 |
| Benguet, Klondike [e] | Hot springs | | | trace | | 588.0 | nil | 21.3 | 348.6 | |
| Benguet, Lutab | Duakan spring | 10 | 78.0 | 6.1 | 0.07 | 3.1 | nil | 95.0 | 240.0 | 115.0 |
| Benguet, Lutab to Kabayan | Roadside spring | 20 | 87.0 | <5.0 | 0.07 | 3.3 | nil | 106.0 | 28.8 | 70.0 |
| Do | Ubub spring | 2 | 22.0 | 13.0 | 0.07 | 2.7 | nil | 26.8 | 132.0 | 100.0 |
| Benguet, Trinidad | Spring near Municipio | 10 | 33.0 | 12.0 | 0.07 | 3.8 | nil | 40.3 | nil | 14.0 |
| Bontoc, Mainit [f] | Spring | | | | | 752.6 | | | 295.4 | |
| Ifugao, Aova | Spring at Km. 76 | 125 | 49.0 | 2.5 | nil | 2.6 | nil | 59.8 | trace | 39.0 |
| Ifugao, Banaue | Bognakan spring | 25 | 100.0 | 32.0 | 0.13 | 3.8 | nil | 122.0 | nil | 85.0 |
| Do | Kiakop spring | | 105.0 | 4.6 | 0.13 | <2.5 | nil | 128.0 | nil | 72.0 |
| Do | Magabon spring | 15 | 120.0 | 18.0 | nil | <2.5 | nil | 146.0 | nil | 105.0 |
| Do | Paypayan spring | 20 | 94.0 | 16.0 | nil | 4.5 | nil | 115.0 | nil | 75.0 |
| Ifugao, Kiangan | Adliang spring | 50 | 160.0 | 13.0 | 0.2 | 2.5 | nil | 195.0 | 24.0 | 150.0 |
| Do | Adukpung spring | 20 | 185.0 | 38.0 | 0.13 | 7.0 | nil | 226.0 | 56.4 | 170.0 |
| Do | Adungbú spring | 20 | 230.0 | 37.0 | 0.33 | 2.5 | nil | 280.0 | 49.2 | 230.0 |
| Do | Atuda spring | 100 | 140.0 | nil | 0.20 | <2.5 | trace | 170.8 | 20.4 | 110.0 |
| Do | Malpao spring (East) | 75 | 230.0 | 21.0 | 0.53 | <2.0 | nil | 280.0 | 78.0 | 220.0 |
| Do | Lakdo spring | 20 | 37.0 | 19.0 | 0.13 | 2.5 | nil | 45.0 | trace | 25.0 |
| Do | Lubungan spring | 150 | 195.0 | 32.0 | 0.13 | 3.0 | nil | 238.0 | 39.6 | 180.0 |
| Do. [g] | Piko spring | 110 | 250.0 | 15.0 | 0.13 | 2.9 | nil | 305.0 | 168.0 | 280.0 |
| Ifugao, Sapao | Bolanan spring | 25 | 50.0 | <2.5 | 0.13 | 2.5 | nil | 61.0 | trace | 43.0 |
| Lepanto, Cervantes [h] | Comilias spring | | 58.0 | 2.3 | 0.14 | 360.0 | nil | 70.0 | 200.0 | 190.0 |
| NUEVA VIZCAYA PROVINCE. | | | | | | | | | | |
| Bagabag | Baños spring | 15 | 195.0 | 15.0 | 0.47 | 8.3 | nil | 238.0 | 19.2 | 190.0 |
| Do | Small pump well | 25 | 160.0 | 32.0 | 4.3 | 12.5 | nil | 195.0 | 21.6 | 150.0 |
| Bambang | Small pump well near Calle Rizal | | 140.0 | 19.0 | 0.13 | 12.5 | nil | 170.8 | 44.4 | 150.0 |
| Bayombong | Bangan spring | 20 | nil | 61.0 | 6.3 | <2.5 | nil | nil | 42.0 | 7.0 |
| Do | Pumping well at plaza | | 130.0 | 5.1 | 1.7 | 10.0 | nil | 159.0 | 24.0 | 140.0 |
| Boscaran | Spring near school | 20 | 240.0 | 23.0 | 1.0 | 3.1 | nil | 293.0 | 103.2 | 210.0 |

[d] Turbidity, 120; total solids, 2,370; silica, 190; aluminium (Al), 7.5; calcium, 180; magnesium (Mg), 26.

[e] Silica, 40.9; calcium, 134; magnesium, trace.

[f] Silica, 195; calcium, 91.07; magnesium (Mg), 0.663; sodium oxide ($Na_2O$), 457; potassium oxide ($K_2O$), 23.1; carbonates ($CO_3$), 208.2.

[g] Turbidity, 10; total solids, 520; silica, 44; aluminium (Al), 5.6; calcium (Ca), 130; magnesium, 19.

[h] Turbidity, 5; total solids, 1,090; silica, 45; aluminium (Al), 3.3; calcium (Ca), 72; magnesium, 3.

TABLE II.—*Chemical analyses of the waters tested for radioactivity*—Continued.

| Location (province, subprovince, and town or district). | Source. | Capacity per minute. | Alkalinity ($CaCO_3$). | Acidity (as $CO_2$). | Iron (Fe). | Chlorides (Cl). | Carbonates (as $Na_2CO_3$). | Bicarbonates ($HCO_3$). | Sulphates ($SO_4$). | Hardness (as $CaCO_3$). |
|---|---|---|---|---|---|---|---|---|---|---|
| NUEVA VIZCAYA PROVINCE. | | *Liters.* | | | | | | | | |
| Noso | Spring | 10 | 100.0 | 6.7 | 0.33 | 2.5 | nil | 122.0 | nil | 82.0 |
| Orioung [i] | do | 10 | 340.0 | nil | 0.6 | 8.0 | 50.0 | 360.0 | trace | 290.0 |
| Salinas [j] | Salt spring | 20 | 3,700.0 | 2,400.0 | 1.8 | 20,000.0 | nil | 4,514.0 | 900.0 | |
| San Luis | Quarry spring | 35 | 210.0 | 17.0 | 0.67 | <2.5 | nil | 256.0 | trace | 170.0 |
| Santa Fé | Spring | 200 | 130.0 | 7.1 | 0.13 | 3.3 | nil | 159.0 | trace | 130.0 |
| Solano | do | 100 | 160.0 | 24.0 | 0.33 | 6.3 | nil | 195.0 | 19.2 | 170.0 |
| Do | Pumping well | | 160.0 | 26.0 | 0.73 | 6.3 | nil | 195.0 | 20.4 | 160.0 |

[i] Turbidity, 90; total solids, 390; silica, 60; aluminium (Al), 2.7; calcium (Ca), 54; magnesium (Mg), 37.

[j] Total solids, 40,000; silica, 110; aluminium (Al), 18; calcium, 900; magnesium, 220.

is generally more radioactive than that from sedimentary deposits.[10]

The geology of the area discussed in this report has unfortunately not been worked out in sufficient detail to justify generalizations; hence it is not feasible at this time to attempt to deduce any definite relations between radioactivity and the geology of the water-bearing strata. The following description by Smith [11] of a typical portion of this region is appended for the sake of completeness:

This region is typically mountainous, and from the character of the relief we must consider it as being in the stage of "topographic youth." * * *

There are two distinct types of topography in the region covered by this paper, and these are directly to be attributed to the character of the geologic formations. In the country to the west of the Polis Range the formations are mainly volcanic, and we find there an irregular, rugged, accentuated relief. The elevations vary from 370 meters to 2,400 meters or more.

East of this range the formations are folded sediments, giving rise to a more regular topography, and in places the hills and mountains are nothing more than tilted blocks of sandstone. On the eastern slopes these present long, gentle inclines, but to the west they form steep escarpments with here and there a saw toothed skyline. As one goes farther to the east, approaching the valley of the Cagayan, the mountains become mere foothills. * * *

A cross section from the west coast at Tagudin northeastward to the edge of Cagayan Valley gives as good a general idea of the formations and structure of the region as one could expect to get by any procedure short of a detailed survey of the whole country. Fig. 2 is a graphic attempt to record my interpretation of the main facts.

Near the west coast we find gently folded shales and sandstone whose inclination increases as we go toward the Malaya Range, being much contorted as we get well into the cañon. The Malaya Range is essentially a mass of porphyry or, to be more exact, andesite. * * *

The town of Cervantes is situated on a small tongue of high ground between the Abra and one of its branches. The underlying rocks are practically the same as those found in the highland on both sides of the town. As we go toward Bontoc we find the same andesitic mass with, however, several large outcroppings of quartz.

When we reach Bagnan and Sagada we find tuffs and reef limestones overlying this igneous mass. . . . .

"From Sagada to Bontoc extrusive rocks, almost entirely andesites and dacites, are encountered but east of Bontoc the formations become very shortly diorite and granite. This belt of granitic rocks is only from 8 to 10 kilometers wide. There is more andesite, or rather a very fine-grained,

[10] One of the most radioactive waters in the lowlands, from Sibul Springs, Bulacan, is also in a calcareous formation, and others high in activity issue from tuffs and conglomerated igneous materials.

[11] Smith, W. D., Notes on a geologic reconnaissance of Mountain Province, Luzon, P. I., *This Journal, Sec. A* (1915), 10, 177–209.

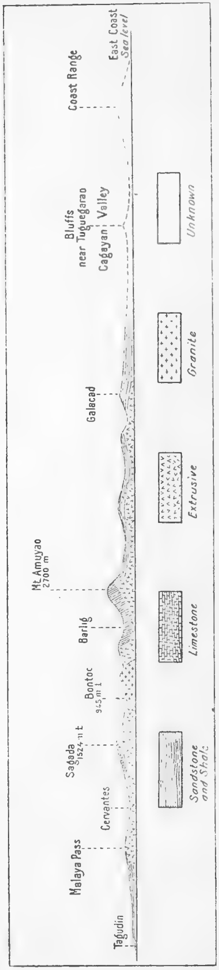


FIG. 2. Generalized geologic section across northern Luzon, from Tagudin to the eastern coast.

almost aphanitic phase of diorite, succeeding the granite on the east as far as the town of Barlig, where steeply dipping sandy shales are encountered. These incline to the southeast.

Sandstone makes up the main mass of Mount Amuyao, and from there east to Cagayan Valley sediments occur. In places, as at Natonin, there are small areas of extrusive rocks overlying the Tertiary sediments.

A comparison of the radioactivity of the waters of the mountains of northern Luzon and that of the waters examined in the Luzon lowlands indicates that the typical lowland waters show the higher radioactivity. The highest radioactivity ($1325 \times 10^{-12}$) determined in the mountains (Adukpung spring, Kiangan) was practically identical with that ($1300 \times 10^{-12}$) of the most active lowland spring (Sinabac spring, Majayjay, Laguna), but considerably less than that ($2100 \times 10^{-12}$) of the most active lowland water (from a flowing well in Batangas, Batangas).

In Nueva Vizcaya the radioactivity encountered was uniformly low, so that the present work has served to emphasize the peculiarity noted last year, that is, a low radioactivity in all waters except those in a small district in Ifugao. Since the waters studied varied greatly, both in chemical quality and in the geological formations from which they were obtained, and since those highly radioactive showed no apparent peculiarities or marked differences from other, less active waters, the high activity of the Ifugao waters seems to be due to isolated local deposits of radioactive material.

The general statements in the literature regarding radioactivity indicate that—

> The phenomenon is perhaps most common among waters of volcanic origin, or at least among thermal springs.[12]

The present study seems to show that this generalization does not hold for Philippine waters, though the work is still too preliminary in character to justify positive statements.

[12] Clarke, F. W., loc. cit., 215.

## ILLUSTRATIONS



TEXT FIGURES

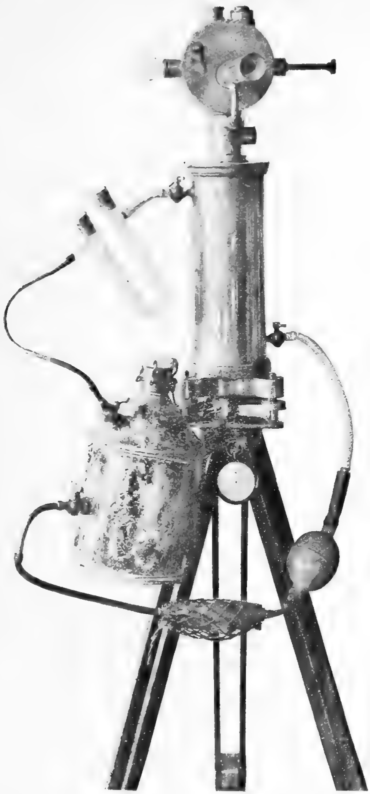

PLATE I. APPARATUS USED IN A FIELD DETERMINATION OF RADIUM EMANATION.

# THE CONSTANCY IN THE RADIOACTIVITY OF CERTAIN PHILIPPINE WATERS [1]

By George W. Heise

*(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila)*

Philippine springs and artesian wells frequently show great variations in flow. Many of them are appreciably augmented during the rainy season, and some, situated near the coast, flow only at high tide. However, so far as noted, the chemical quality of deep-seated ground waters is not subject normally to marked variations, in spite of great fluctuations in the quantity of water.[2] This observation is in harmony with experience in other countries.[3]

The statements regarding the variation in emanation content of natural waters are somewhat confusing. Thus Ramsay [4] reported an increased emanation content in certain springs during periods of wet weather and great flow, whereas Steichen [5] observed an increase in the activity in certain Bombay hot springs during the dry season, in a period of greatly reduced flow. The latter investigator pointed out that local conditions might well account for the differences noted.

In a previous paper [6] it was pointed out that two determinations of the radioactivity of Sibul Springs, one made during the dry season, the other during a period of frequent rains, indicated that, under certain conditions, the seasonal variations might be very slight. Recently it has been found possible to test this conclusion by further work both on Sibul Springs and on a flowing artesian well. Apparatus, method, and limits of accuracy were the some as those previously described.[7] The results obtained are shown in Table I.

[1] Received for publication August, 1917.

[2] Heise, G. W., *This Journal, Sec. A* (1916), **11**, 125–7.

[3] Hintz, F., and Kaiser, E., *Zeitschr. f. prakt. Geol.* (1915), **23**, 122–6, through *Chem. Abst.* (1916), **10**, 1741.

[4] Ramsay, R., The variation of the emanation content of certain springs, *Phil. Mag.* (1915), **30**, 815–818.

[5] Steichen, A., The variation of the hot springs at Tuwa, *Phil. Mag.* (1916), **31**, 401–3.

[6] Wright, J. R., and Heise, G. W., The radioactivity of Philippine waters, *This Journal, Sec. A* (1917), **12**, 145.

[7] Wright and Heise, op. cit. Heise, G. W., The radioactivity of the waters of the mountainous region of northern Luzon, *This Journal, Sec. A* (1917), **12**, No. 6.

TABLE I.—*Variation in radium emanation content.*

| Source. | Date of examination. | Radium emanation content (as g. Ra$\times 10^{-12}$.) |
|---|---|---|
| Sibul Springs | April 10, 1916 | 1284 |
| Do | July 9, 1916 | 1293 |
| Do | April 22, 1917 | 1300 |
| | do | 1280 |
| Do | June 9, 1917 | 1330 |
| Do | July 1, 1917 | 1270 |
| Do | July 15, 1917 | 1280 |
| Flowing well, Parañaque, Rizal | June 19, 1916 | 632 |
| Do | June 2, 1916 | 640 |

The differences between determinations of the radioactivity of the same source at various times are well within the limits of experimental error in this class of work. Though the work on Sibul Springs was done in only a few months in the year, determinations were made under greatly varied conditions. Sibul Springs has a very large flow throughout the year, but the quantity of water changes appreciably with the season. The readings in April, 1916, and April, 1917, were made after prolonged seasons of dry weather, at times of minimum water flow. Though there was no sharply defined rainy season in 1916, the July reading was taken during a period of frequent, though not very heavy, rains, at a time of increased flow. There was much heavier rainfall in 1917 than during the corresponding period in 1916, so that the July, 1917, readings were taken during a time of heavy precipitation and great flow. It is, therefore, reasonable to suppose that the readings noted are representative of the radioactivity of Sibul Springs throughout the year.

The determinations of the activity of the Parañaque flowing well are too few in number to be conclusive; they are so concordant, however, that they may be regarded as corroboratory evidence.

The data at hand clearly indicate, therefore, that the radioactivity of a deep-seated ground water may remain remarkably constant for long periods.

As the waters at Sibul Springs have been highly regarded for a long time because of their supposed medicinal virtues, they have been frequently analyzed. It is of interest to point out that surprisingly little, if any, change has been noted in the chemical character of the water for a long period of time. In

Table II are shown an analysis published by Centeno [8] in 1890 and a recent routine analysis made in the Bureau of Science.

TABLE II.—*Analyses of water from Sibul Springs.*

| Ingredient. | Centeno, 1890.[a] | Analyzed by Bureau of Science, 1915.[b] |
| --- | --- | --- |
| Total solids | 532 | 550 |
| Silica ($SiO_2$) | 30 | 15 |
| Bicarbonates ($HCO_3$) | 477 | 460 |
| Sulphates ($SO_4$) | 13 | nil |
| Chloride (Cl) | 42 | 32 |
| Calcium (Ca) | 153 | 150 |
| Magnesium (Mg) | 17 | 14 |

[a] Recalculated as parts per million and to same terms as those used in standard practice.
[b] Analyzed by F. Peña, chemist, Bureau of Science.

Considering the length of time that has elapsed between the two analyses and the fact that the waters at Sibul Springs were neglected for a year during that interval, better agreement could be hardly expected.

[8] Centeno, J., et al., Memoria descriptiva de los manantiales, etc. de la Isla de Luzon. Madrid (1890), 39.

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